

Sur la valeur d'une distribution dans un point

par

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Dans la communication qui suit nous introduisons la notion de valeur d'une distribution dans un point; nous signalons aussi quelques théorèmes concernant cette notion. Ils seront publiés sous une forme plus développée avec démonstrations dans *Studia Mathematica*.

Nous utiliserons dans la suite les notations de L. Schwartz [2].

1. Considérons une distribution T d'une variable, définie dans un voisinage d'un point x_0 . Si la limite

$$(1) \quad \lim_{\lambda \rightarrow 0} T(x_0 + \lambda x) = C$$

existe dans un voisinage de x_0 et si elle est une distribution constante C^*), nous disons que la distribution T a la valeur

$$T(x_0) = C$$

au point x_0 . Si l'égalité (1) subsiste pour $x \neq 0$ ou seulement pour $x > 0$, nous disons que la distribution T possède la limite $\lim_{x \rightarrow x_0} T$ ou la limite

$\lim_{x \rightarrow x_0+} T$ respectivement. Il est à noter, que L. Schwartz dans [2] (vol. II p. 61) a fait la remarque suivante pour le cas de la notion analogue de la limite à l'infinie: "On peut encore dire qu'une distribution T est bornée, si l'ensemble de ses translatées $\tau_h T$ est borné dans $(\mathcal{D}')$; que T converge vers 0 à l'infinie, si $\tau_h T$ converge vers 0 dans $(\mathcal{D}')$ pour $|h| \rightarrow \infty$ ".

Ces notions ont un caractère local et elles coïncident avec les notions usuelles dans le cas d'une fonction T continue, ou bien ayant une limite au sens usuel.

*) Z. Zieleźny [2] a démontré que la limite (1) est toujours une constante, pourvu qu'elle existe.

L'existence d'une primitive continue F de T , d'ordre n suffisamment grand, possédant au point x_0 une différentielle d'ordre n au sens de Denjoy,

$$T = F^{(n)} \quad \text{et} \quad F(x) = \frac{C}{n!} (x - x_0)^n + o(|x - x_0|^n),$$

est une condition nécessaire et suffisante pour que la valeur de T dans x_0 existe et soit égale à C , c'est-à-dire, à n^e quotients différentiels au sens de Denjoy. Il en résulte que la limite (1) est forte dans $(\mathcal{D}'^p)$ pourvu que p soit suffisamment grand. L'entier p le plus petit possible sera appelé *ordre de la valeur* $T(x_0)$. On a donc

$$T(x_0) = \lim_{\delta \rightarrow 0} (T, \alpha),$$

où (T, α) désigne le produit scalaire, $\alpha \in (\mathcal{D}^p)$ support de $\alpha \subset [x_0 - \delta, x_0 + \delta]$, $\int_{-\infty}^{\infty} \alpha(x) dx = 1$ et $\max |\alpha(p)(x)| = o(1/\delta^{p+1})$, pourvu que l'ordre de $T(x_0)$ ne dépasse pas p .

L'existence de la limite (1) entraîne celle de la limite

$$(1') \quad \lim_{\substack{\lambda \rightarrow 0 \\ \mu \rightarrow 0}} T(x_0 + \lambda x + \mu),$$

si $\mu = 0(\lambda)$. Si $\lambda \rightarrow 0$ et $\mu \rightarrow 0$ d'une façon quelconque, il résulte de l'existence de la limite (1') que T est une fonction continue au point x_0 .

2. Si une distribution T a une valeur au point x_0 , il en est de même de la distribution primitive. Si $\lim_{x \rightarrow x_0 -} T_1 = \lim_{x \rightarrow x_0 +} T_2$, il existe une distribution T telle que $T = T_1$ pour $x < x_0$, $T = T_2$ pour $x > x_0$ et $T(x_0) = \lim_{x \rightarrow x_0 -} T_1 = \lim_{x \rightarrow x_0 +} T_2$.

On a toujours au sens défini ci-dessus pour $\alpha, \beta > 0$ $\lim_{x \rightarrow 0} |x|^{-\alpha} \sin |x|^{-\beta} = 0$ (cf. aussi un exemple de Denjoy [1], p. 277). La fonction $|x|^{-\alpha} \sin |x|^{-\beta}$ peut donc être considérée comme une distribution dans l'intervalle $(-\infty, \infty)$ qui a la valeur 0 pour $x = 0$. Cette valeur est d'ordre exactement égal à $E(\alpha/\beta) + 1$. En choisissant convenablement α et β , nous obtenons donc une fonction sommable dont la valeur est d'ordre arbitrairement grand.

Si α est une fonction suffisamment régulière, $\alpha(x_0) = 0$, $\lim_{x \rightarrow x_0} T = 0$, et si l'on fait une hypothèse sur la croissance de α , la règle de De l'Hôpital subsiste:

$$\lim_{x \rightarrow x_0} T/\alpha = \lim_{x \rightarrow x_0} T'/\alpha';$$

en outre, non seulement l'existence du membre droit entraîne ici celle du membre gauche, mais aussi réciproquement. On a, par exemple,

$$T'(x_0) = \lim_{x \rightarrow x_0} \frac{T(x) - T(x_0)}{x - x_0},$$

pourvu que le membre droit ou gauche existe. Enfin, on en tire le corollaire que, pour chaque distribution T , on a $(Ta)(x_0)=0$, lorsque $a(x_0)=\dots=a^{(k)}(x_0)=0$, k étant suffisamment grand.

La dérivée usuelle au point x_0 de la primitive d'une fonction sommable f est la valeur de f en x_0 ; les deux notions coïncident lorsque la fonction f est bornée inférieurement ou supérieurement. Dans le cas général, la valeur de f peut cependant être d'ordre aussi grand que l'on veut.

3. Une distribution qui possède une valeur en tout point (d'un intervalle) y est déterminée par ces valeurs, c'est-à-dire si $T(x)=0$, pour tout x , on a $T=0$; (sous l'hypothèse que l'ordre de la valeur $T(x)$ soit borné, c'est une conséquence d'un théorème de Denjoy [1], p. 319-320). Cela résulte du théorème suivant:

Si $T(x) \geq 0$ pour tout x , alors $T \geq 0$ (au sens de la théorie des distributions [2]).

Si T possède une valeur en tout point, on peut considérer la fonction $f(x)=T(x)$; cette fonction est de 1^{re} classe de Baire et a la propriété de Darboux. Si la fonction $f(x)$ est sommable, on a $T=f$ (au sens des distributions).

L'hypothèse que la valeur $T(x)$, qui existe en tout x , peut être remplacée par l'hypothèse que cette valeur $T(x)$ existe sauf dans un ensemble dénombrable et que la primitive de T possède une valeur partout.

4. On peut définir à l'aide de la notion de valeur le produit scalaire de deux distributions et l'intégrale (définie). Posons en effet

$$(T, S) = (T * \check{S})(0),$$

où $\check{S}$ est la distribution S après substitution $u=-x$, et

$$\int_a^b T dx = (T, \chi_{[a, b]}),$$

où $\chi_{[a, b]}(x)$ est la fonction caractéristique de l'intervalle $[a, b]$.

Généralisons ensuite les règles usuelles, l'intégration par parties, par exemple. La dernière définition équivaut à celle de Zieleźny [3]: $\int_a^b T dx$ est la valeur de la distribution $T_1(x+b) - T_1(x+a)$ au point $x=0$, pourvu qu'elle existe, où T_1 est une primitive de T .

Les théorèmes signalés (voir 3.) fournissent un nouveau mode de traiter les fonctions comme des distributions, ce qui permet d'intégrer par exemple les fonctions telles que $1/|x|^a \sin 1/|x|^b$, qui ne sont pas intégrales au sens de Denjoy. Cette correspondance entre fonctions et distributions se laisse prolonger (par induction transfinie) de façon à obtenir une généralisation de l'intégrale de Denjoy.

5. La définition de la valeur d'une distribution en un point pour plusieurs variables est analogue et elle donne lieu à des théorèmes analogues. Mais ce qui est plus intéressant, c'est la possibilité de définir la fixation des variables. À savoir, si la limite

$$\lim_{\lambda \rightarrow 0} T(x_0 + \lambda x, y)$$

existe, elle est une distribution $T(x)$ indépendante de x ; on dit alors qu'elle résulte de la distribution $T(x, y)$ par fixation de la variable $x = x_0$. On peut définir ensuite le produit scalaire, l'intégrale sur une région, et généraliser par exemple le théorème de Green-Gauss-Ostrogradsky. On a enfin la définition suivante du produit multiplicatif de deux distributions:

$$TS = (T(x) \times S(y))_{x=y}.$$

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On Certain Theorems of the Mercer Type

by

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In the theory of Hausdorff transformations [1], [2], the regularity of the summability method is usually investigated with the aid of the theory of moments. For instance, in 1938 H. R. Pitt [4] obtained, by the method of Mellin transforms, the necessary and sufficient condition under which regular Hausdorff's summability method sums only convergent sequences. However, in certain cases, theorems of this type can be proved without the use of the analytical method, by using only Cauchy's theorem for complex sequences, which corresponds to l'Hopital's rule for functions.

If $\mu_n = W_1(n)/W(n)$, where $W(x)$ is a polynomial of degree k , $W_1(x)$ is of degree $l \leq k$, $W(n) \neq 0$ and $W(0) = W_1(0)$, then it is possible to show by the above method that the necessary and sufficient condition for the regularity of Hausdorff's summability method, corresponding to the sequence $\{\mu_n\}$, is that the real parts of all the roots of equation $W(x) = 0$ be negative.

In the proof of this theorem we make use of the following two properties of Hausdorff's transforms $\{t_n\}$ of the sequence $\{s_n\}$:

$$(1) \quad \text{If } \mu_n = (-1)^k \binom{n}{k}, \text{ then } t_n = \begin{cases} 0 & \text{for } n < k, \\ \binom{n}{k} \Delta^k s_{n-k} & \text{for } n \geq k. \end{cases}$$

$$(2) \quad \text{If } W(x) \text{ is a polynomial of degree } k, \mu_n = W(n) \text{ and } s_n = \binom{n}{r} = \frac{n!}{r!(n-r)!}, \text{ then } t_n = W(r) \binom{n}{r} \text{ for } n \geq k.$$

As an application of the above theorem we obtain the following theorem of the Mercer type: Let $p_n = as_n + (1-a)t_n$, $a \neq 0$, $W(n) \neq 0$ for $n = 0, 1, 2, \dots$ and let the sequence $\mu_n = 1/W(n)$ correspond to the transformation of the sequence $\{s_n\}$ into the sequence $\{t_n\}$; the assumption $\lim p_n = s$ implies the equality $\lim s_n = s$ if and only if the real parts of

all roots of the equation $W(x)=1-1/a$ are negative. In this theorem, and in those that follow, we assume that $|s| < \infty$.

In the case of Cesàro transforms $c_n^{(k)}$ and Hölder transforms $h_n^{(k)}$ of integral order there exist constants a'_k and a''_k respectively, such that the condition $\lim p_n = s$ implies $\lim s_n = s$ if and only if $a > a'_k$ resp. $a > a''_k$. Both sequences are increasing for $k \geq 2$, non-negative and convergent to the value $\frac{1}{2}$. The following asymptotic representations are true:

$$a'_k \sim \frac{1}{2} - \frac{1}{48} \frac{\pi^4}{\ln^2 k},$$

$$a''_k = \frac{\cos^k \frac{\pi}{k}}{1 + \cos^k \frac{\pi}{k}} \sim \frac{1}{2} - \frac{\pi^2}{8k}.$$

The first of the theorems given above implies not only the Mercierian theorems, but almost immediately the following theorem of Tauber as well: if $\lim c_n^{(k)} = s$ and $\lim na_n = 0$, then $\lim s_n = s$, where $s_n = \sum_{v=0}^n a_v$.

Analogous theorems can be formulated in the case of Hausdorff difference transforms of the function $f(x)$, which are defined by the formula

$$t(x) = \sum_{n=0}^{\infty} \mu_n \binom{x}{n} \Delta^n f(0);$$

here $f(x)$ is a complex function of a real variable.

It will be observed that the Cesàro transform $c_k(x)$ of the function $f(x)$ defined by the equality

$$c_k(x) = \frac{1}{\binom{x+k}{k}} \sum_{n=0}^{\infty} \binom{n+k-1}{k-1} f(x-n)$$

is a Hausdorff transform with $\mu_n = \frac{1}{\binom{n+k}{k}}$ provided the series in the

numerator is convergent and the function $c_k(x)$ can be represented by its Newton-Gregory series. Similarly, in the case of the Hölder transforms defined by the equalities $h_1(x) = c_1(x)$, $h_k(x) = h_1[h_{k-1}(x)]$ for $k = 2, 3, \dots$ we have $\mu_n = 1/(n+1)^k$.

Now let us consider the Hausdorff differential transforms defined by the formula

$$t(x) = \sum_{n=0}^{\infty} \mu_n \frac{x^n}{n!} f^{(n)}(0).$$

Applying l'Hôpital's rule to the case of complex functions of a real variable we can prove theorems analogous to those in the first two cases.

The investigation of the regularity of the three types of Hausdorff transformations here presented leads to a discussion of the asymptotic properties of solutions of linear difference equations for sequences and functions and of differential equations of the Euler type. In the case of sequences it is easy to ascertain that property (1) of Hausdorff transforms, p. 243, implies that the transform $\{t_n\}$ corresponding to the sequence with terms $\mu_n = W_1(n)/W(n)$ satisfies the difference equation

$$(*) \quad L(x_n) = L^*(s_n), \quad \text{where} \quad L(x_n) = \sum_{v=0}^k \lambda_v \binom{n}{v} \Delta^v x_{n-v},$$

$$L^*(x_n) = \sum_{v=0}^k \eta_v \binom{n}{v} \Delta^v x_{n-v}, \quad \lambda_v = (-1)^v \Delta^v W(0),$$

$$\eta_v = (-1)^v \Delta^v W_1(0), \quad W(0) = W_1(0).$$

Thus the theorem given at the beginning results from the following theorem: The difference equation $(*)$ has a solution $\{x_n\}$ convergent to s if $\lim s_n = s$ and if all the real parts of the roots r_v of the characteristic equation $W(x) = 0$ are different from 0. The condition $R(r_v) < 0$ for $v = 1, 2, \dots, k$ is necessary and sufficient for all solutions of the difference equation $(*)$ to be convergent to s . It will be observed that the equation $L(x_n) = 0$ is the difference equivalent of Euler's differential equation.

This fact suggests that each solution of the difference equation $(*)$ can be regarded as a transform of the sequence $\{s_n\}$. In the case $R(r_v) \neq 0$, $v = 1, 2, \dots, k$, the summability method represented by $(*)$ can be regarded as regular, by which we mean that if $\lim s_n = s$ there exists a transform $\{x_n\}$ satisfying $(*)$ and convergent to s .

If $L^*(s_n) = s_n$, we can state the following theorem, which is a generalization of the previous one: Let $L(x_n) = x_n + \sum_{v=1}^k \lambda_v(n) \Delta^v x_{n-v}$; we assume that the homogeneous difference equation $L(x_n) = 0$ has linearly independent solutions $\alpha_n^{(j)}$, $j = 1, 2, \dots, k$, for which $W_n^{(j)} \neq 0$ and

$$(a) \quad |W_n^{(j)}| \rightarrow \infty \quad \text{and} \quad \sum_{v=0}^{n-1} |\Delta W_v^{(j)}| \leq K |W_n^{(j)}|;$$

or

$$(b) \quad W_n^{(j)} \rightarrow 0 \quad \text{and} \quad \sum_{v=n}^{\infty} |\Delta W_v^{(j)}| \leq K |W_n^{(j)}|,$$

where

$$W_n^{(j)} = \frac{\begin{vmatrix} 1 & a_n^{(1)} & \dots & a_n^{(j-1)} \\ 1 & a_{n-1}^{(1)} & \dots & a_{n-1}^{(j-1)} \\ \dots & \dots & \dots & \dots \\ 1 & a_{n-j+1}^{(1)} & \dots & a_{n-j+1}^{(j-1)} \end{vmatrix}}{\begin{vmatrix} a_n^{(1)} & a_n^{(2)} & \dots & a_n^{(j)} \\ a_{n-1}^{(1)} & a_{n-1}^{(2)} & \dots & a_{n-1}^{(j)} \\ \dots & \dots & \dots & \dots \\ a_{n-j+1}^{(1)} & a_{n-j+1}^{(2)} & \dots & a_{n-j+1}^{(j)} \end{vmatrix}} \quad \text{for } j = 2, 3, \dots, k,$$

$$W_n^{(1)} = \frac{1}{a_n^{(1)}}.$$

If $\lim s_n = s$, then there exists a solution $\{x_n\}$ of the difference equation $L(x_n) = s_n$ convergent to s . If $|W_n^{(j)}| \rightarrow \infty$ for $j = 1, 2, \dots, k$, then each solution has this property.

Analogous theorems can be formulated for the case of functional linear difference equations and differential equations [3], [5].

Detailed proofs of the above theorems will be published in the *Annales Polonici Mathematici*.

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Sur l'allure asymptotique des solutions d'équation du type parabolique

par

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1. Soit

$$(1) \quad \mathcal{L}[u] \equiv a(x, t) u''_{xx} + b(x, t) u'_x + c(x, t) u - u'_t = 0$$

une équation linéaire homogène du type parabolique à coefficients continus à l'intérieur de la demi-bande $\Sigma: 0 \leq x \leq 1, t \geq 0$. Supposons que $a(x, t) > 0, c(x, t) \leq 0$ à l'intérieur de Σ . Nous allons démontrer le théorème suivant:

THÉORÈME 1 *). Supposons l'existence d'une fonction $V(x, t)$ régulière **)
dans Σ et telle que

$$1^\circ \quad V(x, t) > 0 \text{ dans } \Sigma,$$

$$2^\circ \quad \mathcal{L}[V] \leq 0 \text{ à l'intérieur de } \Sigma,$$

$$3^\circ \quad \lim_{t \rightarrow \infty} V(x, t) = 0 \text{ uniformément par rapport à } x \text{ pour } 0 \leq x \leq 1.$$

Soit $u(x, t)$ une solution de l'équation (1), régulière dans Σ et satisfaisant aux conditions

$$(2) \quad \lim_{t \rightarrow \infty} u(0, t) = 0, \quad \lim_{t \rightarrow \infty} u(1, t) = 0.$$

On a alors

$$\lim_{t \rightarrow \infty} u(x, t) = 0$$

uniformément par rapport à x pour $0 \leq x \leq 1$.

*) Les recherches de l'auteur concernant l'allure asymptotique des solutions des équations paraboliques ont été inspirées par un problème posé par l'ingénieur A. Lewandowski. Les résultats concernant les problèmes analogues et se rattachant au phénomène de congélation ont été exposés dans le travail de L. Rubinstein [2]. L'idée de la démonstration de l'un des théorèmes du travail précité a influencé celle du théorème 1 publié dans la présente note.

**) C'est-à-dire continue dans Σ et ayant les secondes dérivées continues à l'intérieur de Σ .

Démonstration. Soit δ un nombre positif arbitraire. Considérons la fonction

$$\bar{u}(x, t) = u(x, t) - \delta - kV(x, t),$$

où k est un nombre constant positif qui sera convenablement choisi dans la suite. On a

$$(3) \quad \mathcal{L}[\bar{u}] = -c(x, t)\delta - k\mathcal{L}[V] \geq 0.$$

D'après l'hypothèse (2), il existe un nombre positif T_0 tel que l'on a

$$(4) \quad |u(0, t)| < \delta, \quad |u(1, t)| < \delta \quad \text{pour} \quad t > T_0.$$

Choisissons le nombre k de façon à avoir

$$(5) \quad \bar{u}(x, 0) < 0 \quad \text{pour} \quad 0 \leq x \leq 1$$

et

$$\bar{u}(0, t) < 0, \quad \bar{u}(1, t) < 0 \quad \text{pour} \quad 0 \leq t \leq T_0.$$

On a d'après (4)

$$(6) \quad \bar{u}(0, t) < 0, \quad \bar{u}(1, t) < 0 \quad \text{pour} \quad t \geq 0.$$

Il résulte du théorème connu sur les extrema des solutions de l'équation du type parabolique ([3], [4]) que les inégalités (5) et (6) entraînent l'inégalité $\bar{u}(x, t) \leq 0$ dans Σ , c'est-à-dire

$$(7) \quad u(x, t) \leq \delta + kV(x, t) \quad \text{pour} \quad (x, t) \in \Sigma.$$

On démontre d'une manière analogue que le nombre k étant choisi convenablement, on a

$$(8) \quad u(x, t) \geq -\delta - kV(x, t) \quad \text{pour} \quad (x, t) \in \Sigma.$$

Il résulte de (7) et (8) que l'on a

$$(9) \quad |u(x, t)| \leq \delta + kV(x, t) \quad \text{pour} \quad (x, t) \in \Sigma,$$

à condition que le nombre k soit assez élevé.

Ceci établi, choisissons le nombre $T_1 > 0$ tel que l'on ait

$$(10) \quad V(x, t) < \delta, k \quad \text{pour} \quad t > T_1.$$

On a d'après (9) et (10)

$$(11) \quad |u(x, t)| < 2\delta \quad \text{pour} \quad t > T_1.$$

Or, le nombre $\delta > 0$ étant arbitraire, il résulte de (11) que $\lim_{t \rightarrow \infty} u(x, t) = 0$ uniformément par rapport à x pour $0 \leq x \leq 1$.

Le théorème 1 est ainsi démontré.

REMARQUE. Si, ϱ étant un nombre positif, inférieur à $1/2$, on remplace l'hypothèse 3° par la suivante:

on a $\lim_{t \rightarrow \infty} V(x, t) = 0$ pour $0 \leq x \leq 1$ uniformément par rapport à $x \in [\varrho, 1 - \varrho]$,
 on démontre de la même façon que $\lim_{t \rightarrow \infty} u(x, t) = 0$ pour $0 \leq x \leq 1$ uniformément par rapport à $x \in [\varrho, 1 - \varrho]$.

2. Passons à la détermination effective de la fonction $V(x, t)$ satisfaisant aux hypothèses du théorème 1. Les hypothèses du n-ro 1 sur les coefficients de l'équation (1) restant valables, supposons que le coefficient $a(x, t)$ soit supérieur à un nombre positif a_0 et que le coefficient $b(x, t)$ soit borné supérieurement à l'intérieur de Σ . Soient enfin B un nombre positif tel que l'on ait $b(x, t) \leq B$ à l'intérieur de Σ et K — un nombre positif quelconque.

Étant donnée, une solution $z(x)$ de l'équation différentielle ordinaire

$$(12) \quad a_0 z'' + Bz' + K = 0,$$

régulière pour $0 \leq x \leq 1$ (c'est-à-dire continue pour $0 \leq x \leq 1$ et ayant la seconde dérivée continue pour $0 < x < 1$), et jouissant des propriétés

$$(13) \quad z(x) > 0 \text{ pour } 0 \leq x \leq 1, \quad z'(x) \geq 0, \quad z''(x) \leq 0 \text{ pour } 0 < x < 1,$$

on a d'après (12) et (13)

$$(14) \quad a(x, t)z'' + b(x, t)z' + c(x, t)z \leq a_0 z'' + Bz' = -K \\ \text{pour } 0 < x < 1 \quad \text{et} \quad t > 0.$$

Pour déterminer la solution $z(x)$ de l'équation (12) qui jouisse des propriétés (13), écrivons l'intégrale générale de cette équation sous la forme suivante:

$$(15) \quad z = -C_0 \exp\left(-\frac{B}{a_0}x\right) - \frac{K}{B}x + C_1.$$

Alors

$$z' = \frac{BC_0}{a_0} \exp\left(-\frac{B}{a_0}x\right) - \frac{K}{B}.$$

En posant

$$C_0 = \frac{Ka_0}{B^2} \exp \frac{B}{a_0},$$

on a

$$z' = \frac{K}{B} \left[\exp \frac{B}{a_0} (1-x) - 1 \right]$$

et par suite $z'(x) \geq 0$ pour $0 < x < 1$. D'autre part,

$$z'' = -\frac{K}{a_0} \exp \frac{B}{a_0} (1-x) \leq 0 \quad \text{pour} \quad 0 < x < 1.$$

En posant dans (15)

$$C_1 = \frac{K}{B} \left(2 + \frac{a_0}{B} \exp \frac{B}{a_0} \right),$$

on aura l'inégalité $z(x) \geq K/B > 0$.

Les coefficients C_0 et C_1 étant ainsi choisis, la fonction $z(x)$ jouira des propriétés (13) et par suite on aura (14). De plus, elle est bornée dans l'intervalle $[0, 1]$. Posons

$$(16) \quad V(x, t) = z(x) e^{-\lambda t},$$

où λ est un nombre positif que nous allons convenablement choisir. On a

$$e^{\lambda t} \mathcal{L}[V] = a(x, t) z'' + b(x, t) z' + c(x, t) z + \lambda z$$

et on déduit de (14) l'inégalité

$$(17) \quad e^{\lambda t} \mathcal{L}[V] \leq \lambda z(x) - K.$$

Soit z_0 la borne supérieure de $z(x)$ dans l'intervalle $[0, 1]$. Posons $\lambda = K/2z_0$. On a alors, vu (17), l'inégalité $\mathcal{L}[V] < 0$ à l'intérieur de Σ . D'autre part, $V(x, t) > 0$ dans Σ en vertu de (13) et (16).

Nous avons construit ainsi la fonction $V(x, t)$ satisfaisant aux hypothèses du théorème 1. Il en résulte le théorème suivant:

THÉORÈME 2. *Supposons que les coefficients de l'équation (1) soient continus à l'intérieur de la demi-bande Σ et que l'on ait $a(x, t) \geq a_0$, $c(x, t) \leq 0$, a_0 étant un nombre constant positif; le coefficient $b(x, t)$ est supposé borné supérieurement à l'intérieur de Σ .*

Soit $u(x, t)$ une solution de l'équation (1), régulière dans Σ et satisfaisant aux conditions (2).

On a alors $\lim_{t \rightarrow \infty} u(x, t) = 0$ uniformément par rapport à x pour $0 \leq x \leq 1$.

3. Considérons l'équation linéaire du type parabolique de la forme

$$(18) \quad \mathcal{L}_1[V] \equiv a(x) v''_{xx} + b(x) v'_x + c(x) v - v'_t = f(x)$$

et admettons que les coefficients et la fonction $f(x)$ y sont continus dans l'intervalle $[0, 1]$. Soient en outre $a(x) > 0$ et $c(x) \leq 0$ pour $0 \leq x \leq 1$. On déduit aussitôt du théorème 2 le théorème suivant:

THÉORÈME 3. *Soit $v(x, t)$ une solution de l'équation (18), régulière dans la demi-bande Σ et satisfaisant aux conditions*

$$(19) \quad \lim_{t \rightarrow \infty} v(0, t) = l_0, \quad \lim_{t \rightarrow \infty} v(1, t) = l_1.$$

Soit $w(x)$ une solution de l'équation différentielle

$$(20) \quad a(x) w'' + b(x) w' + c(x) w = f(x),$$

régulière dans l'intervalle $[0,1]$ et satisfaisant aux conditions aux limites

$$(21) \quad w(0)=l_0, \quad w(1)=l_1.$$

On a alors $\lim_{t \rightarrow \infty} v(x,t)=w(x)$ uniformément par rapport à $x \in [0,1]$.

Pour la démonstration, il suffit d'observer que la fonction $u(x,t)=v(x,t)-w(x)$ constitue une solution régulière dans Σ de l'équation homogène $\mathcal{L}_1[V]=0$ et d'appliquer à cette fonction le théorème 2.

4. Le théorème 3 s'étend aux équations non-linéaires de la forme

$$(22) \quad F(x,t,v,v'_x,v''_{xx})-v'_t=0,$$

la fonction $F(x,t,v,p,r)$ et les dérivées F'_v, F'_p, F'_r étant continues par rapport à ses arguments pour $0 < x < 1, t > 0, -\infty < v < +\infty, -\infty < p < +\infty, -\infty < r < +\infty$. Admettons en outre que $F'_r \geq a_0 > 0, F'_v \leq 0$ et que la dérivée F'_p soit bornée supérieurement. Soit $v(x,t)$ une solution de l'équation (22), régulière dans la demi-bande Σ et satisfaisant aux conditions (19). Soit $w(x)$ une solution de l'équation différentielle

$$F(x,t,w,w'_x,w''_{xx})=0,$$

régulière dans l'intervalle $[0,1]$ et satisfaisant aux conditions (21). Posons enfin $u(x,t)=v(x,t)-w(x)$. On a alors

$$F(x,t,v,v'_x,v''_{xx})-F(x,t,w,w',w'')=a(x,t)u''_{xx}+b(x,t)u'_x+c(x,t)u,$$

les coefficients $a(x,t), b(x,t)$ et $c(x,t)$ étant continus à l'intérieur de Σ (voir [1]), les coefficients $a(x,t)$ et $c(x,t)$ y satisfaisant aux inégalités $a(x,t) \geq a_0 > 0$ et $c(x,t) \leq 0$, et le coefficient $b(x,t)$ y étant borné supérieurement. Comme $u'_t=v'_t$, la fonction $u(x,t)$ est une solution de l'équation de la forme (1) dont les coefficients satisfont aux hypothèses du théorème 2. On déduit aussitôt de ce théorème que $\lim_{t \rightarrow \infty} u(x,t)=0$ et par suite que $\lim_{t \rightarrow \infty} v(x,t)=w(x)$ uniformément par rapport à $x \in [0,1]$.

INSTITUT MATHÉMATIQUE DE L'ACADÉMIE POLONAISE DES SCIENCES

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Calculus of Approximations

by

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Presented by H. STEINHAUS on February 6, 1956

This paper presents a theory which lays down the foundations for numerical computations and makes it possible to formulate properly many numerical problems.

By the approximate number $[a, A]$ we shall indicate the interval $[a, A]$, i. e. the set of all real numbers x that satisfy the inequality $a \leq x \leq A$.

The approximate number $[B - b, B + b]$ can also be denoted by $\overset{b}{B}$. Thus,

the approximate number $[a, A]$ can be expressed in the form $\overset{\frac{1}{2}(A-a)}{\frac{1}{2}(A+a)}$. We shall omit initial zeros in the upper part, if they lie to the left of the

last digit of the lower one. For example, we shall write $\overset{02}{3.1416}$ instead of $\overset{0.00002}{3.1416}$.

We say that the approximate numbers a and β are equal and we write $a = \beta$ if, and only if, they are two identical intervals. Hence, we have $\overset{a}{[a, A]} = \overset{b}{[b, B]}$ if, and only if, $a = b$ and $A = B$, and similarly $\overset{a}{A} = \overset{b}{B}$ if, and only if, $A = B$ and $a = b$.

We say that the approximate number β approximates the approximate number a and we write $a \Rightarrow \beta$ or $\beta \Leftarrow a$, if, and only if, the interval β includes the interval a . Thus, we have $\overset{a}{[a, A]} \rightarrow \overset{b}{[b, B]}$ if, and only if, $a \geq b$ and $A \leq B$, and similarly $\overset{a}{A} \rightarrow \overset{b}{B}$ if, and only if, $b - a \geq |B - A|$. It is easy to prove that the approximations $a \rightarrow \beta$ and $\beta \Rightarrow \gamma$ imply $a \rightarrow \gamma$.

The relation $a \Rightarrow \beta$ is a partial ordering of the set of all approximate numbers.

In practical computations it is convenient to use the following two rules:

the rounding-off rule: $\overset{a}{A} + c \Rightarrow \overset{a+|c|}{A}$;

the extending rule: $\overset{a}{A} \Rightarrow \overset{b}{A}$ if $b \geq a$.

For example,

$$\begin{array}{ccc} & 09 & 0189 & 02 \\ 2.7182 & \Rightarrow 2.72 & \Rightarrow 2.72 & . \end{array}$$

Here the lower part 2.7182 has been rounded off at first to 2.72 by means of the rounding-off rule, and afterwards the upper part 0.00189 has been rounded off to 0.002 by means of the extending rule.

We say that the approximate number γ is the sum, the difference, the product, or the quotient of the approximate numbers a and β , and we write $a + \beta = \gamma$, $a - \beta = \gamma$, $a \cdot \beta = \gamma$, or $a : \beta = \gamma$ respectively if, and only if, γ is the set of all numbers $x + y$, $x - y$, xy or x/y respectively, where x is a real number from the interval a and y a real number from

the interval β . In place of $a : \beta$ we also write $\frac{a}{\beta}$. We assume that the interval β does not include zero, whenever it is a divisor. In that case, if $\beta = [b, B]$, then $bB > 0$, and if $\beta = B$, then $b < |B|$.

It can be proved that

$$[a, A] + [b, B] = [a + b, A + B], \quad \frac{a}{A} + \frac{b}{B} = \frac{a + b}{A + B},$$

$$[a, A] - [b, B] = [a - B, A - b], \quad \frac{a}{A} - \frac{b}{B} = \frac{a - b}{A - B},$$

$$[a, A] \cdot [b, B] = [\min(ab, aB, Ab, AB), \max(ab, aB, Ab, AB)],$$

$$\frac{a}{A} \cdot \frac{b}{B} = \frac{|A| |b + a| B| + ab - \min(|A| |b, a| B|, ab)}{\operatorname{sgn}(AB) [|AB| + \min(|A| |b, a| B|, ab)]},$$

$$[a, A] : [b, B] = \left[\min \left(\frac{a}{b}, \frac{a}{B}, \frac{A}{b}, \frac{A}{B} \right), \max \left(\frac{a}{b}, \frac{a}{B}, \frac{A}{b}, \frac{A}{B} \right) \right],$$

$$\frac{a}{A} : \frac{b}{B} = \frac{a}{A} \cdot \frac{b}{B} \cdot \frac{0}{B^2 - b^2}.$$

For example,

$$\begin{array}{ccc} 2 & 7 & 91 + 14 \\ (-13) \cdot 3 = (-39 + 6) = & 105 & \\ & (-45) & . \end{array}$$

Approximate numbers do not form a group with respect to addition,

because the equation $\frac{a}{A} + \xi = \frac{b}{B}$ has no solution whenever $b < a$. Moreover, subtraction is not the inverse operation of addition, that is, the equality

$\frac{a}{A} + \frac{b}{B} - \frac{b}{B} = \frac{a}{A}$ does not hold whenever $b \neq 0$, but $\frac{a}{A} + \frac{b}{B} - \frac{b}{B} = \frac{a + 2b}{A + B}$.

Similarly, division is not the inverse operation of multiplication. It is a consequence of the irreversible process of error accumulation.

Addition and multiplication are both commutative and associative, but the distributive laws fail for multiplication and division. However, the relations

$$a \bullet (\beta - \gamma) \Rightarrow a \bullet \beta - a \bullet \gamma, \quad a \bullet (\beta - \gamma) \Rightarrow a \bullet \beta - a \bullet \gamma,$$

$$(a + \beta) \div \gamma \Rightarrow a \div \gamma + \beta \div \gamma, \quad (a - \beta) \div \gamma \Rightarrow a \div \gamma - \beta \div \gamma$$

hold. Therefore, we say that multiplication and division are weakly distributive with respect to addition and subtraction.

We can also multiply or divide approximate numbers in an approximate number by using the following formulas:

$$A \bullet B \Rightarrow \frac{a + \frac{|A|}{|B|}b}{\frac{|B|}{|B|} - b} \quad , \quad A \div B \Rightarrow \frac{a}{B} \quad ;$$

these formulas are very convenient in practical computations.

The set of all approximate numbers, the upper part of which equals zero, that is, the set of approximate numbers which are intervals reduced to points, is isomorphic to the set of all real numbers with respect to the arithmetical operations. We shall denote the isomorphism by writing $\overset{0}{A} = A$.

The definition of approximate numbers and of the operations on them given above are not sufficient in practical computations. Although the operations were defined in a natural way, they are not regular enough (multiplication and division are not distributive with respect to addition and subtraction) and the inverse operations fail. Therefore we shall now extend the conception of an approximate number and introduce some new operations in order to obtain a ring of approximate numbers.

From now on we shall indicate by the approximate number $[a, A]$ the interval $[\min(a, A), \max(a, A)]$ with the sense from a to A or reduced to a point, if $a = A$. Thus, there is now no need to assume $a \leq A$.

The approximate number $[B - b, B + b]$ may also be denoted by $\overset{b}{B}$, but now $b \geq 0$ is not assumed.

If $a \leq A$, we shall call the approximate number $[a, A]$ a positively oriented interval or simply an interval. If $a \geq A$, it will be called a negatively oriented interval. Thus $\overset{b}{B}$ is an interval if, and only if, $b \geq 0$.

If $b \leq 0$, $\overset{b}{B}$ is a negatively oriented interval. We shall identify the appro-

ximate numbers in the previous sense with the intervals in the new sense. All the natural operations will hold for the intervals.

We now define equality, approximation and the four regular arithmetical operations for all approximate numbers as follows:

$$[a, A] = [b, B] \quad \text{if, and only if,} \quad a = b, \quad A = B, \quad \text{i. e.} \quad \overset{a}{A} = \overset{b}{B} \quad \text{if,} \\ \text{and only if,} \quad A = B, \quad a = b,$$

$$[a, A] \Rightarrow [b, B] \quad \text{if, and only if,} \quad a \geq b, \quad A \leq B, \quad \text{i. e.} \quad \overset{a}{A} \Rightarrow \overset{b}{B} \quad \text{if,} \\ \text{and only if,} \quad b - a \geq |B - A|,$$

$$[a, A] + [b, B] = [a + b, A + B], \quad \text{i. e.} \quad \overset{a}{A} + \overset{b}{B} = \overset{a+b}{A+B},$$

$$[a, A] - [b, B] = [a - b, A - B], \quad \text{i. e.} \quad \overset{a}{A} - \overset{b}{B} = \overset{a-b}{A-B},$$

$$[a, A] \cdot [b, B] = [ab, AB], \quad \text{i. e.} \quad \overset{a}{A} \cdot \overset{b}{B} = \overset{aB+Ab}{AB+ab},$$

$$[a, A] : [b, B] = \left[\frac{a}{b}, \frac{A}{B} \right] \quad \text{if } b \neq 0, \quad B \neq 0, \quad \text{i. e.} \quad \overset{a}{A} : \overset{b}{B} = \frac{\overset{aB-Ab}{B^2-b^2}}{\overset{AB-ab}{B^2-b^2}} \quad \text{if } |B| \neq b.$$

We see that the natural addition of intervals is identical with regular addition.

Approximate numbers form a ring with respect to addition and regular multiplication. Regular subtraction and division are the inverse operations of addition and regular multiplication respectively. All the approximate numbers $[0, A]$ and $[a, 0]$, i. e. all the approximate numbers $\overset{a}{A}$ with $|A| = |a|$, are divisors of zero in the ring, but they do not form an ideal, because every approximate number is a sum of two divisors of zero: $[a, A] = [a, 0] + [0, A]$.

Every approximate number is a linear combination of the approximate numbers $\overset{0}{1}$ and $\overset{1}{0}$. Therefore, approximate numbers form a two-dimensional linear vector space with respect to addition, and regular multiplication by real numbers.

The set of all approximate numbers $\overset{0}{A}$ is isomorphic to the set of all real numbers with respect to the regular arithmetical operations.

We denote the isomorphism, as before, by writing $\overset{0}{A} = A$. Every approximate number $\overset{a}{A}$ can be written in the form $A + \overset{1}{a}A$, where $A = \overset{1}{0}$ ($A^2 =$

$=AA=1$). Thus we may compute with approximate numbers (excepting the division by a divisor of zero) in a similar manner as with complex numbers. For example:

$$5 \cdot 6 = (5 + 3A) (6 - 2A) = 30 - 10A + 18A - 6A^2 = 24 + 8A = 24.$$

Approximate numbers can be represented by points in a plane. Let (X, x) be the rectangular Cartesian co-ordinates of a point P in the plane. We say that the point P represents the approximate number $X + xA$. In such a way we have a one-to-one correspondence between the approximative numbers and the points on a plane.

If $|a| < |A|$, then the approximate number $\overset{a}{A}$ can be written in the form $\varrho(\text{ch } \psi + A \text{ sh } \psi)$, where the modulus ϱ and the argument ψ are real, $\varrho = \pm \sqrt{A^2 - a^2}$. We call this the hyperbolic form of the approximate number $\overset{a}{A}$. If $|a| > |A|$, ϱ and ψ are complex. If $|a| = |A|$, that is if $\overset{a}{A}$ is a divisor of zero, it cannot be written in a hyperbolic form. It is easy to verify that, as with complex numbers in the trigonometric form, the modulus of the regular product of two approximate numbers is the product of their moduli and the argument of the product is the sum of the arguments. The modulus of the regular quotient of two approximate numbers is the quotient of their moduli and the argument of the quotient is the argument of the numerator minus the argument of the denominator. As in De Moivre's theorem, if n is a positive integer, then $[\varrho(\text{ch } \psi + A \text{ sh } \psi)]^n = \varrho^n(\text{ch } n\psi + A \text{ sh } n\psi)$.

All the natural operations can be translated into the regular ones. For example,

$$\overset{a}{A} \cdot \overset{b}{B} = \begin{cases} a \text{ sgn } B - b \text{ sgn } A & \\ A : B & \text{if } |A| \geq a \geq 0, |B| \geq b \geq 0, \\ a \text{ sgn } B & \text{if } |A| \leq a, |B| \geq b \geq 0. \\ A : (B - b \text{ sgn } B) & \end{cases}$$

In many numerical problems it is convenient to operate in the following way. Formulate the problem by use of the natural operations; afterwards translate these operations into the regular ones, and then solve the problem by their use.

Many numerical problems reduce to a system of approximations. We compute with approximations in a manner similar to that used for equations or inequalities in the usual algebra.

In order to introduce a topology into the ring of approximate numbers we now define a norm. By the norm of an approximate number

$\alpha = \overset{a}{A}$ we mean the real number $\|\alpha\| = |A| + |a|$. Such a norm has all the

required properties and besides $\|a \cdot \beta\| \leq \|a\| \cdot \|\beta\|$. Thus, approximate numbers form a two-dimensional Banach algebra with respect to addition, regular multiplication and regular multiplication by real numbers.

A sequence of approximate numbers $\{a_n\}$ is said to be convergent to a if, and only if, it converges in the norm, i. e. $\lim_{n \rightarrow \infty} \|a_n - a\| = 0$. Thus, it follows that

$$\lim_{n \rightarrow \infty} [a_n, A_n] = [\lim_{n \rightarrow \infty} a_n, \lim_{n \rightarrow \infty} A_n] \quad \text{and} \quad \lim_{n \rightarrow \infty} a_n = \lim_{n \rightarrow \infty} A_n.$$

We shall call a function with real arguments and approximate values, an approximate function. For example, let $F(x)$, $f(x)$ and $G(x)$ be three usual functions of the real variable x , such that $|G(x) - F(x)| \leq f(x)$.

Then we say that the approximate function $\overset{f(x)}{F}(x)$ approximates the function $G(x)$ and we write

$$G(x) \Rightarrow \overset{f(x)}{F}(x).$$

We define continuity, convergence, derivative and integral of an approximate function $\overset{f(x)}{\varphi}(x) = \overset{f(x)}{F}(x)$ in the obvious way, and the following formulas result:

$$\overset{f'(x)}{\varphi'}(x) = \overset{f'(x)}{F'}(x), \quad \int_a^b \overset{f(x)}{\varphi}(x) dx = \int_a^b \overset{f(x)}{F}(x) dx.$$

$$\text{If } \overset{f(x)}{F}(x) \Rightarrow \overset{g(x)}{G}(x) \quad \text{and} \quad g(x_0) = 0, \quad \text{then} \quad \overset{f'(x_0)}{F'}(x_0) \Rightarrow \overset{g'(x_0)}{G'}(x_0).$$

$$\text{If } \varphi(x) \Rightarrow \psi(x), \quad \text{then} \quad \int_a^b \varphi(x) dx \Rightarrow \int_a^b \psi(x) dx.$$

We shall call a function with approximate arguments and values a function of approximate variables. For example, the approximate value of the integral $\int_x^X f(u) du$, where $f(u)$ is a fixed usual function of a real variable u , is a function of the interval $[x, X]$, if the method of computing is uniquely defined.

Continuity, convergence, derivatives and integrals of functions of approximate variables are introduced in a manner similar to the analogous conceptions for functions of complex variables. They have many

interesting properties, which, however, seem to be of no great use in numerical problems.

The author of this paper has elaborated the details of the theory outlined above. He is preparing a monograph. All the numerical methods and computations can be written in the language of this theory; many new methods arise; many cumbersome computations can be performed automatically. There are many numerical problems which cannot be formulated properly, because this theory fails.

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES

Une remarque sur la méthode de Banach-Cacciopoli-Tikhonov dans la théorie des équations différentielles ordinaires

par

A. BIELECKI

Présenté par T. WAŻEWSKI le 1 Mars 1956

Dans les théorèmes d'existence et d'unicité des solutions des équations différentielles on applique assez souvent [1], [2], [3] une méthode qui s'appuie sur le théorème suivant bien connu de Banach-Cacciopoli-Tikhonov:

Si la transformation $\tilde{\varphi}=F(\varphi)$, définie sur tout l'espace métrique et complet E , satisfait aux conditions

$$(I) \quad F(E) \subset E,$$

$$(II) \quad \delta(F(\varphi), F(\psi)) \leq q \cdot \delta(\varphi, \psi),$$

où $0 < q < 1$ et $\delta(\varphi, \psi)$ désigne la distance des éléments φ et ψ de l'espace E , il existe un élément invariant $\varphi_0 = F(\varphi_0) \in E$.

Si l'on applique dans les théorèmes d'existence et d'unicité des solutions des équations différentielles ordinaires le théorème de Banach-Cacciopoli-Tikhonov comme on le fait usuellement, on gagne en clarté, en comparaison avec la méthode classique des approximations successives, et on abrège les calculs, mais, d'autre part, on n'obtient pas de résultats plus forts; au contraire, il est nécessaire d'introduire d'avance des conditions supplémentaires imposant des limitations aux intervalles dans lesquels les solutions doivent être définies.

On peut pourtant remédier à cet inconvénient si l'on introduit convenablement la métrique de l'espace fonctionnel E ; nous allons le montrer par un simple exemple, en considérant une équation différentielle du premier ordre.

Nous admettons que la fonction $f(x, y)$ est définie et continue dans le domaine

$$(D) \quad \begin{aligned} 0 &\leq x < a \leq +\infty \\ -\infty &< y < +\infty, \end{aligned}$$

et qu'elle y satisfait aux conditions

$$(1) \quad |f(x, \bar{y}) - f(x, \bar{y})| \leq L(x) |\bar{y} - \bar{y}|,$$

$$(2) \quad |f(x, 0)| \leq L(x),$$

où $L(x)$ est une fonction non négative et continue dans l'intervalle $[0, \alpha)$ *).

Nous remplaçons l'équation différentielle

$$(3) \quad \frac{d\varphi(x)}{dx} = f(x, \varphi(x))$$

avec la condition initiale $\varphi(0) = \eta$ par l'équation intégrale équivalente,

$$(4) \quad \varphi(x) = \int_0^x f(t, \varphi(t)) dt + \eta,$$

dont les solutions sont assujetties à la condition de continuité.

Nous désignons par E l'espace des fonctions $\varphi(x)$ définies et continues dans l'intervalle $[0, \alpha)$ et satisfaisant à la condition

$$(5) \quad \sup_{0 \leq x < \alpha} \{ |\varphi(x)| e^{-\kappa \int_0^x L(u) du} \} = \|\varphi\| < +\infty,$$

avec la métrique

$$(6) \quad \delta(\varphi, \psi) = \sup_{0 \leq x < \alpha} \{ |\varphi(x) - \psi(x)| e^{-\kappa \int_0^x L(u) du} \} = \|\varphi - \psi\|,$$

où κ est un nombre positif fixe. On démontre sans peine que E est un espace métrique complet.

La transformation

$$(7) \quad \tilde{\varphi}(x) = F(\varphi) = \int_0^x f(t, \varphi(t)) dt + \eta,$$

définie sur tout l'espace E , remplit la condition (I). En effet, si $\varphi(x) \in E$, on a, d'après (1), (2) et (5),

$$\begin{aligned} |\tilde{\varphi}(x)| &\leq \int_0^x \{ L(t) |\varphi(t)| + |f(t, 0)| \} dt + |\eta| \leq \\ &\leq \frac{\|\varphi\| + 1}{\kappa} \int_0^x \kappa L(t) e^{\kappa \int_0^t L(u) du} dt + |\eta| \leq \frac{\|\varphi\| + 1}{\kappa} e^{\kappa \int_0^x L(t) dt} + |\eta| \leq \left(\frac{\|\varphi\| + 1}{\kappa} + |\eta| \right) e^{\kappa \int_0^x L(t) dt}, \end{aligned}$$

*) En particulier, si $L = \text{const}$, la fonction $f(x, y)$ est bornée pour $y = 0$ et satisfait à la condition de Lipschitz par rapport à y . On peut évidemment ramener à ce cas celui où la fonction $f(x, y)$ est définie dans un rectangle fermé et borné.

où

$$\|\tilde{\varphi}(\kappa)\| \leq \frac{\|\varphi\| + 1}{\kappa} + |\eta| < +\infty.$$

et par suite $\tilde{\varphi}(x) \in E$.

De plus

$$\begin{aligned} |F(\varphi) - F(\psi)| &\leq \int_0^x L(t) |\varphi(t) - \psi(t)| dt \leq \frac{1}{\kappa} \int_0^x \kappa L(t) e^{\kappa \int_0^t L(u) du} \delta(\varphi, \psi) dt = \\ &= \frac{1}{\kappa} (e^{\kappa \int_0^x L(u) du} - 1) \cdot \delta(\varphi, \psi), \end{aligned}$$

d'où

$$\delta(F(\varphi), F(\psi)) \leq \frac{1}{\kappa} \delta(\varphi, \psi).$$

La condition (II) sera donc aussi remplie, si l'on suppose que $\kappa > 1$ *). Ainsi, on peut appliquer le théorème de Banach-Cacciopoli-Tikhonov et il existe un élément invariable $\varphi_0(x)$ de la transformation (7), appartenant à E et satisfaisant à l'équation (4) dans l'intervalle $[0, a)$ tout entier **).

La méthode que nous avons exposée s'applique sans modifications essentielles aux systèmes d'équations différentielles ordinaires du premier ordre. On l'applique aussi aisément aux équations intégrales du type

$$(8) \quad \varphi(x) = \int_0^x f(x, t, \varphi(t)) dt + g(x),$$

ou aux systèmes d'équations de cette espèce. Avec une métrique convenablement choisie elle se prête aussi à l'étude d'équations plus compliquées, telles que

$$\varphi(x) = \int_0^x f\left(x, t, \varphi(t), \int_0^t \varphi(u) du\right) dt,$$

etc.

Pour terminer, nous allons indiquer encore une variante de la méthode exposée. L'équation (3) avec la condition $\varphi(0) = \eta$ est équivalente à l'équation intégrale

$$(9) \quad \psi(x) = f\left(x, \int_0^x \psi(t) dt + \eta\right),$$

*) M. J. Kiszyński a remarqué que, dans le cas où $a < +\infty$ et la fonction $L(t)$ est bornée, il suffit d'admettre $\kappa = 1$.

**) En appliquant la métrique habituelle $\delta(\varphi, \psi) = \sup |\varphi(x) - \psi(x)|$, nous serions obligés, même dans le cas où $L = \text{const}$, d'assujettir a priori l'intervalle $[0, a)$ à la condition supplémentaire $aL < 1$.

où $\varphi(x) = d\varphi(x)/dx$. L'équation (9) peut aussi être traitée par la méthode de Banach-Cacciopoli-Tikhonov si l'on pose

$$\|\varphi(x)\| = \sup_{0 \leq x < a} \frac{\int_0^x |\varphi(t)| dt}{e^{\frac{x}{k} \int_0^x L(t) dt}}, \quad (k > 1).$$

De même qu'auparavant, on obtient la solution dans l'intervalle $[0, a)$ tout entier.

L'application d'une méthode analogue aux équations aux dérivées partielles fait l'objet de la communication suivante [4].

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Une remarque sur l'application de la méthode de Banach-Cacciopoli-Tikhonov dans la théorie de l'équation $s=f(x,y,z,p,q)$

par

A. BIELECKI

Présenté par T. WAŻEWSKI le 1 Mars 1956

Dans la communication précédente [2] nous avons fait quelques remarques méthodologiques sur les applications du théorème de Banach sur le point fixe [1] aux démonstrations des théorèmes d'existence et d'unicité des solutions des équations différentielles ordinaires; nous y avons montré par un exemple comment il était possible, en choisissant convenablement la métrique d'un espace fonctionnel auxiliaire, d'améliorer la méthode usuelle et de faire disparaître les limitations, résultant d'elle seule, auxquelles sont assujettis les intervalles d'existence des solutions, ce qui diminue quelque peu la valeur de la méthode Banach-Cacciopoli-Tikhonov en comparaison avec la méthode classique des approximations successives. Dans cette note, nous allons indiquer un exemple analogue relatif à la théorie des équations aux dérivées partielles.

Nous admettons que la fonction $f(x,y,z,p,q)$ est définie et continue dans le domaine

$$(D) \quad 0 \leq x < \alpha \leq +\infty, \quad 0 \leq y < \beta \leq +\infty, \quad -\infty < z, p, q < +\infty,$$

et qu'elle y satisfait aux conditions

$$(1) \quad |f(x,y,\bar{z},\bar{p},\bar{q}) - f(x,y,\bar{z},\bar{p},\bar{q})| \leq L(x,y) \{|\bar{z}-z| + |\bar{p}-p| + |\bar{q}-q|\},$$

$$(2) \quad |f(x,y,0,0,0)| \leq L(x,y),$$

où $L(x,y)$ et ses dérivées partielles $L'_x(x,y)$ et $L'_y(x,y)$ sont continues et non négatives dans le domaine

$$(A) \quad 0 \leq x < \alpha, \quad 0 \leq y < \beta.$$

Il s'agit de démontrer, moyennant ces hypothèses, qu'il existe une fonction $z=\varphi(x,y)$, et une seule, définie et continue dans A , ayant dans

ce domaine des dérivées continues $p(x, y) = \partial\varphi/\partial x$, $q(x, y) = \partial\varphi/\partial y$ et $s(x, y) = \partial^2\varphi/\partial x\partial y = \partial^2\varphi/\partial y\partial x$ satisfaisant dans ce domaine à l'équation aux dérivées partielles

$$(3) \quad s = f(x, y, z, p, q)$$

et aux conditions initiales

$$(4) \quad \varphi(0, 0) = 0,$$

$$(5) \quad p(x, 0) = q(0, y) = 0^*).$$

Pour la démonstration nous utiliserons le théorème du point fixe de Banach. Nous allons montrer qu'en choisissant convenablement la métrique d'un espace fonctionnel auxiliaire il est possible de supprimer les conditions supplémentaires imposées au domaine d'existence de la solution, qui apparaissent si l'on applique le théorème de Banach de la manière usuelle.

Considérons $s(x, y)$ comme la fonction inconnue. Notre tâche se ramène, de façon bien connue, au problème de l'existence et de l'unicité de la solution de l'équation intégrale

$$(6) \quad s(x, y) = f\left(x, y, \int_0^x \int_0^y s(u, v) du dv, \int_0^y s(x, v) dv, \int_0^x s(u, y) du\right),$$

où la solution $s(x, y)$ est assujettie à la condition d'être continue dans le domaine Δ .

Nous introduirons les notations suivantes: si $\varphi(x, y)$ est une fonction continue dans le domaine Δ , alors

$$\Psi(x, y) = \int_0^x \int_0^y |\varphi(u, v)| du dv + \int_0^y |\varphi(x, v)| dv + \int_0^x |\varphi(u, y)| du,$$

$$\Lambda(x, y) = \int_0^x \int_0^y L(u, v) du dv + \int_0^y L(x, v) dv + \int_0^x L(u, y) du,$$

$$\|\varphi(x, y)\| = \sup_{\substack{0 \leq x < \alpha \\ 0 \leq y < \beta}} \{\Psi(x, y) e^{-\kappa \Lambda(x, y)}\}, \quad \kappa > 0.$$

Désignons par E l'ensemble des fonctions $\varphi(x, y)$ définies et continues dans Δ , et satisfaisant à la condition $\|\varphi\| < +\infty$. L'ensemble E est un espace de Banach **). La transformation fonctionnelle

$$(7) \quad \tilde{\varphi}(x, y) = F(\varphi) = f\left(x, y, \int_0^x \int_0^y \varphi(u, v) du dv, \int_0^y \varphi(x, v) dv, \int_0^x \varphi(u, y) du\right)$$

*) Il est bien connu que les conditions initiales plus générales $\varphi(0, 0) = \xi$, $p(x, 0) = \sigma(x)$, $q(0, y) = \tau(y)$ peuvent être ramenées aux conditions (4) et (5).

**) C'est-à-dire un espace linéaire, normé et complet.

transforme l'espace E en un sous-ensemble de celui-ci:

$$(8) \quad F(E) \subset E.$$

En effet, si $\psi \in E$, alors

$$\begin{aligned} \tilde{\Psi}(x, y) &\leq \int_0^x \int_0^y \{L(u, v) \Psi(u, v) + |f(u, v, 0, 0, 0)|\} du dv + \\ &+ \int_0^y \{L(x, v) \Psi(x, v) + |f(x, v, 0, 0, 0)|\} dv + \int_0^x \{L(u, y) \Psi(u, y) + |f(u, y, 0, 0, 0)|\} du \\ &\leq \frac{\|\psi\| + 1}{\kappa} \left\{ \int_0^x \int_0^y \kappa L(u, v) e^{\kappa A(u, v)} du dv + \int_0^y \kappa L(x, v) e^{\kappa A(x, v)} dv \right. \\ &\quad \left. + \int_0^x \kappa L(u, y) e^{\kappa A(u, y)} du \right\} \leq \\ &\leq \frac{\|\psi\| + 1}{\kappa} \left\{ \int_0^x \int_0^y \frac{\partial^2}{\partial u \partial v} (e^{\kappa A(u, v)}) du dv + \right. \\ &\quad \left. + \int_0^y \frac{\partial}{\partial v} (e^{\kappa A(x, v)}) dv + \int_0^x \frac{\partial}{\partial u} (e^{\kappa A(u, y)}) du \right\} \leq 3 \cdot \frac{\|\psi\| + 1}{\kappa} e^{\kappa A(x, y)}. \end{aligned}$$

De là

$$(9) \quad \|\tilde{\psi}\| = \|F(\psi)\| \leq 3 \frac{\|\psi\| + 1}{\kappa} < +\infty;$$

$\tilde{\psi} = F(\psi)$ appartient donc à E . On démontre tout de même que, si ψ_1 et ψ_2 appartiennent à E , on a

$$(10) \quad \|F(\psi_1) - F(\psi_2)\| \leq \frac{3}{\kappa} \|\psi_1 - \psi_2\|.$$

Supposons que $\kappa > 3$. En tenant compte de (8) et (10), nous pouvons appliquer le théorème de Banach et arrivons à la conclusion qu'il existe exactement une fonction $s(x, y)$, définie et continue dans A , invariante par rapport à la transformation (7). Elle satisfait donc à l'équation intégrale (6).

Le raisonnement se simplifie considérablement si l'on suppose que la fonction f est bornée, $L = \text{const.}$ et A est un domaine borné fermé. C'est à ce cas que l'on peut ramener celui où l'équation (3) est donnée dans un parallélépipède rectangle fermé et borné.

La méthode exposée dans ce travail s'applique aussi, sans modifications essentielles, à un autre problème classique, où les conditions initiales sont données le long d'une ligne qui a au plus un point commun avec chaque caractéristique.

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Cross-Section of the Methyl Mercaptan Molecule for the Scattering of Slow Neutrons

by

W. KOŁOS

Presented by L. INFELD on March 8, 1956

In previous papers [2], [3] we calculated the cross-section of the methyl alcohol molecule for the scattering of slow neutrons. Agreement with experiment could be obtained when, besides rotation and hindered rotation, the influence of vibrations of the protons was taken into account. However, the model used in the calculations was still simplified, e. g. the association of the molecules in the liquid state was neglected, although it follows from spectroscopical data that in liquid methyl alcohol there are practically no single molecules, but only associated ones.

It is obvious that when intermolecular bindings in the associated complexes are sufficiently strong to hinder the rotation of single molecules, the cross-sections of the protons are greater than in the case of freely rotating molecules. However, this effect may be disturbed because the energy of the first excitation of the hydrogen bond $\text{O}-\text{H}\cdots\text{O}$ is only of the order 200 cm.^{-1} , and thereby is smaller than the energy of thermal neutrons.

In the previous papers we were able only to estimate the influence of vibrations on the proton cross-section. Therefore it was not possible to conclude whether it follows from our agreement with experiment that the molecules in the associated complexes are bound in such a manner that the bondings have no influence on the scattering of slow neutrons and the molecules may be regarded as free, or whether there is an influence of the association on the proton cross-section which was compensated by a wrong estimation of the influence of vibrations.

To answer this question it is necessary to carry out further experiments and calculations for other molecules. That is why we have now calculated the cross-section of the methyl mercaptan molecule.

The theory developped in the previous papers [2], [3] was used, and the cross-sections of the protons were calculated from the formula

$$(1) \quad \sigma_{m_i} = \frac{4\sigma_0(\mu_0\mu_1\mu_2\mu_3)^{1/2}}{I_{m_i}} \sum_{\tau_f} b_0^2(\tau_i, \tau_f) \sum_{n=0}^{\infty} \frac{(-1)^n D_{n+\tau_{if}}}{n!(2\tau_{if}+n)!},$$

where

$$(2) \quad D_n = \frac{(2n)!(s+n)!(8\mu'E_i a^2/\hbar^2)^n}{(n!)^2(n+1)} \sum_{m=0}^{2p} \gamma_m \frac{(d+m+n)!}{(d+s+m+2n+1)!},$$

which was derived in [3] *), where the notation is also explained.

The coefficients b_0 are given by

$$(3) \quad b_0(\tau_i, \tau_f) = \sum_{m=-\infty}^{\infty} a_m^{(\tau_i)} a_m^{(\tau_f)},$$

where $a_m^{(\tau_i)}$ and $a_m^{(\tau_f)}$ are the coefficients of the Fourier expansion of the periodic part of the Mathieu function for the initial and final states respectively. Only elastic collisions with respect to the hindered rotation are considered.

Some values of the b_0^2 coefficients calculated for the potential barrier $H = 705$ cal./mole [1] are given in Table I.

TABLE I

$\tau_i \longleftrightarrow \tau_f$		$0 \longleftrightarrow 1$	$0 \longleftrightarrow 2$	$0 \longleftrightarrow 3$	$0 \longleftrightarrow 4$	$0 \longleftrightarrow 5$	$0 \longleftrightarrow 6$	$0 \longleftrightarrow 7$
b_0^2	in CH_3	0.978	0.939	0.884	0.805	0.723	0.624	0.521
	in SH	0.945	0.828	0.663	0.449	0.320	0.203	0.116

The resulting cross-section of the methyl mercaptan molecule is shown in Fig. 1.

In [3] we assumed the influence of vibrations on the cross-section of the methyl alcohol molecule to be the same as for the methane molecule. With the same assumption we obtain for the methyl mercaptan molecule the cross-section which is shown in Fig. 2 as a function of the initial neutron energy.

If there were no influence of association on the proton cross-section it might be expected that experiment would give, for the cross-section,

*) In this paper there is a misprint in the formula itself. The numerical calculations were, nevertheless, made according to the correct formula.

values which are in agreement with our curve in Fig. 2, or, for thermal neutrons, a slightly smaller one, similar to that obtained for the methyl alcohol molecule [3].

However, if there were an influence of association on the proton cross-section, then the experimentally measured cross-section would be different from that calculated above, and the effect of association would be shown by this difference. This would be mainly the effect of the

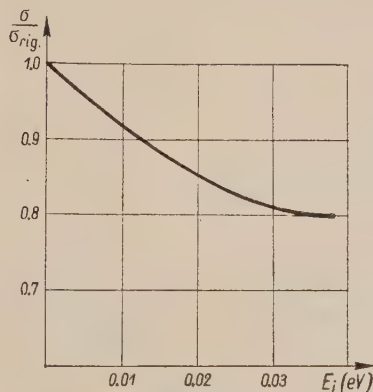


Fig. 1.

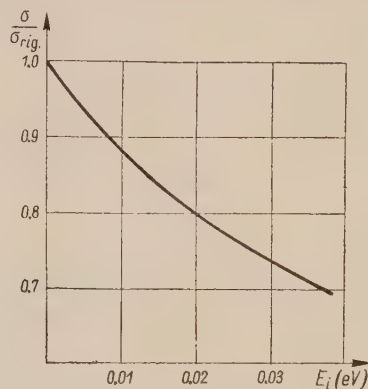


Fig. 2.

Fig. 1. Cross-section of the methyl mercaptan molecule accounting for the influence of rotation and hindered rotation, in units of the cross-section of the rigid molecule, as a function of the initial neutron energy

Fig. 2. Cross-section of Fig. 2 accounting additionally for the influence of vibrations

association of the methyl alcohol molecules because the binding energy of the hydrogen bond $S-H\cdots S$ is much smaller than that of the $O-H\cdots O$ bond, and for the latter the energy of the first excitation is of the same order of magnitude as the energy of the neutrons.

My thanks are due to Dr. R. W. Kilb for sending me a copy of his "Tables of Mathieu Eigenvalues and Eigenfunctions for Special Boundary Conditions", and to Mr. L. Wolniewicz for his help in numerical calculations.

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Two-Centre Integrals Over the Atomic Sphere

by

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Presented by L. INFELD on March 20, 1956

Fletcher and Wohlfarth [1], [2] in their pioneer work on the tight binding method for $3d$ electrons in nickel have calculated the necessary energy integrals as two-centre integrals.

Atomic $3d$ electron functions have been approximated by linear combinations of Slater's functions. Every integral was calculated as the difference of the integral over all space less the integral over the atomic sphere of the central atom. The radius R of this sphere was taken equal to half the distance between the central atom and its neighbour.

The explicit formulae for the Coulomb two-centre integrals of $3d$ electrons calculated over the forementioned sphere will be presented below.

The $3d$ functions are:

$$\Psi d\sigma = A(5/16\pi)^{1/2}(3z^2 - r^2)e^{-ar},$$

$$\Psi d\pi = A(15/4\pi)^{1/2}xz e^{-ar},$$

$$\Psi d\bar{\delta} = A(15/4\pi)^{1/2}xy e^{-ar}.$$

The integrals to be calculated over the atomic sphere are essentially:

$$\left. \begin{array}{l} (dd\sigma) \\ (dd\pi) \\ (dd\bar{\delta}) \end{array} \right\} = -\frac{15}{4\pi} \int_{r \leq R} d_3 x A e^{-ar} \frac{1}{r'} B e^{-br'} \times \begin{array}{l} \frac{1}{12} (3z^2 - r^2)(3z'^2 - r'^2) \\ (xz)(x'z') \\ (xy)(x'y') \end{array},$$

where a , b are the exponents, and A , B are constant coefficients.

Primed co-ordinates have their origin in the neighbouring atom, unprimed in the central one. We introduce the spheroidal co-ordinates after K. Rüdénberg [3]:

$$x = x' = R[(\xi^2 - 1)(1 - \eta^2)]^{1/2} \cos \varphi,$$

$$y = y' = R[(\xi^2 - 1)(1 - \eta^2)]^{1/2} \sin \varphi,$$

$$z = R(1 - \xi\eta),$$

$$z' = R(1 + \xi\eta),$$

$$r = R(\xi - \eta),$$

$$r' = R(\xi + \eta),$$

$$d_3x = R^3(\xi^2 - \eta^2) d\xi d\eta d\varphi,$$

$$z' = 2R - z.$$

We use the abbreviations:

$$a = R(a + b),$$

$$\beta = R(b - a),$$

and

$$\sigma = a + \beta.$$

The integrals in spheroidal co-ordinates are

$$\left. \begin{aligned} -(dd\sigma) \\ (dd\pi) \\ -(dd\delta) \end{aligned} \right\} = ABR^6 \int_0^1 d\eta \int_1^{1+\eta} d\xi e^{-a\xi - \beta\eta} (\xi - \eta) \times$$

$$\times \begin{cases} (5/8)[9\xi^4\eta^4 - 6(\xi^4\eta^2 + \xi^2\eta^4) + \xi^4 + \eta^4 + 4\xi^2\eta^2 - 6(\xi^2 + \eta^2) + 9] \\ (15/4)[\xi^4\eta^4 - \xi^4\eta^2 - \xi^2\eta^4 + \xi^2 + \eta^2 - 1] \\ (15/16)[\xi^4\eta^4 - 2(\xi^4\eta^2 + \xi^2\eta^4) + \xi^4 + \eta^4 + 4\xi^2\eta^2 - 2(\xi^2 + \eta^2) + 1]. \end{cases}$$

Explicit formulae for $a \neq b$, that is $\beta \neq 0$, are

$$\begin{aligned} (dd\sigma) = & -\frac{5}{2}ABR^6 \frac{e^{-a}}{a} \left\{ \frac{1}{\beta} \left[1 - \frac{1}{\beta} - \frac{4}{\beta^2} + \frac{12}{\beta^3} + \frac{24}{\beta^4} - \frac{120}{\beta^5} + 24 \frac{e^{-\beta}}{\beta^3} \left(1 + \frac{4}{\beta} + \frac{5}{\beta^2} \right) \right. \right. \\ & + \frac{1}{a} \left(-1 + \frac{2}{\beta} - \frac{12}{\beta^2} + \frac{24}{\beta^3} + \frac{168}{\beta^4} - \frac{720}{\beta^5} + 24 \frac{e^{-\beta}}{\beta^2} \left(1 + \frac{7}{\beta} + \frac{23}{\beta^2} + \frac{30}{\beta^3} \right) \right) \\ & + \frac{4}{a^2} \left(-1 - \frac{12}{\beta^2} + \frac{24}{\beta^3} + \frac{216}{\beta^4} - \frac{720}{\beta^5} - 6 \frac{e^{-\beta}}{\beta} \left(1 - \frac{20}{\beta^2} - \frac{84}{\beta^3} - \frac{120}{\beta^4} \right) \right) \\ & + \frac{6}{a^3} \left(1 - \frac{1}{\beta} - \frac{28}{\beta^2} + \frac{36}{\beta^3} + \frac{504}{\beta^4} - \frac{1080}{\beta^5} - 4e^{-\beta} \left(1 + \frac{7}{\beta} + \frac{20}{\beta^2} - \frac{144}{\beta^4} - \frac{270}{\beta^5} \right) \right) \\ & + \frac{6}{a^4} \left(5 - \frac{1}{\beta} - \frac{60}{\beta^2} + \frac{36}{\beta^3} + \frac{1080}{\beta^4} - \frac{1080}{\beta^5} - 4e^{-\beta} \left(4 + \frac{23}{\beta} + \frac{84}{\beta^2} + \frac{144}{\beta^3} - \frac{270}{\beta^5} \right) \right) \\ & + \frac{30}{a^5} \left(1 - \frac{12}{\beta^2} + \frac{216}{\beta^4} - 4e^{-\beta} \left(1 + \frac{6}{\beta} + \frac{24}{\beta^2} + \frac{54}{\beta^3} + \frac{54}{\beta^4} \right) \right) \Bigg\} \\ & - \frac{1}{\sigma} \left[1 - \frac{2}{\sigma} - \frac{4}{\sigma^2} - \frac{18}{\sigma^3} - \frac{162}{\sigma^4} + \frac{7560}{\sigma^6} + \frac{45360}{\sigma^7} + \frac{90720}{\sigma^8} - e^{-\sigma} \left(9 + \frac{102}{\sigma} + \frac{716}{\sigma^2} \right. \right. \\ & + \frac{3726}{\sigma^3} + \frac{14958}{\sigma^4} + \frac{45360}{\sigma^5} + \frac{98280}{\sigma^6} + \frac{136080}{\sigma^7} + \frac{90720}{\sigma^8} \Bigg) \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{\alpha} \left(-1 - \frac{2}{\sigma} - \frac{6}{\sigma^2} - \frac{108}{\sigma^3} - \frac{450}{\sigma^4} + \frac{2160}{\sigma^5} + \frac{27000}{\sigma^6} + \frac{90720}{\sigma^7} + \frac{90720}{\sigma^8} \right. \\
& - e^{-\sigma} \left(33 + \frac{322}{\sigma} + \frac{2028}{\sigma^2} + \frac{9558}{\sigma^3} + \frac{34110}{\sigma^4} + \frac{89640}{\sigma^5} + \frac{163080}{\sigma^6} + \frac{181440}{\sigma^7} \right. \\
& \left. \left. + \frac{90720}{\sigma^8} \right) \right) + \frac{2}{\alpha^2} \left(-2 + \frac{3}{\sigma} - \frac{15}{\sigma^2} - \frac{198}{\sigma^3} - \frac{216}{\sigma^4} + \frac{5400}{\sigma^5} + \frac{29160}{\sigma^6} + \frac{45360}{\sigma^7} \right. \\
& - 2e^{-\sigma} \left(23 + \frac{192}{\sigma} + \frac{1086}{\sigma^2} + \frac{4518}{\sigma^3} + \frac{13662}{\sigma^4} + \frac{28620}{\sigma^5} + \frac{37260}{\sigma^6} + \frac{22680}{\sigma^7} \right) \\
& + \frac{6}{\alpha^3} \left(1 + \frac{4}{\sigma} - \frac{25}{\sigma^2} - \frac{144}{\sigma^3} + \frac{288}{\sigma^4} + \frac{4320}{\sigma^5} + \frac{9720}{\sigma^6} - 2e^{-\sigma} \left(15 + \frac{108}{\sigma} + \frac{550}{\sigma^2} \right. \right. \\
& \left. \left. + \frac{1962}{\sigma^3} + \frac{4734}{\sigma^4} + \frac{7020}{\sigma^5} + \frac{4860}{\sigma^6} \right) \right) \\
& + \frac{6}{\alpha^4} \left(5 + \frac{4}{\sigma} - \frac{60}{\sigma^2} - \frac{144}{\sigma^3} + \frac{1080}{\sigma^4} + \frac{4320}{\sigma^5} - 4e^{-\sigma} \left(9 + \frac{58}{\sigma} + \frac{264}{\sigma^2} + \frac{774}{\sigma^3} + \frac{1350}{\sigma^4} \right. \right. \\
& \left. \left. + \frac{1080}{\sigma^5} \right) \right) + \frac{30}{\alpha^5} \left(1 - \frac{12}{\sigma^2} + \frac{216}{\sigma^4} - 4e^{-\sigma} \left(1 + \frac{6}{\sigma} + \frac{24}{\sigma^2} + \frac{54}{\sigma^3} + \frac{54}{\sigma^4} \right) \right) \Bigg\}.
\end{aligned}$$

$$\begin{aligned}
(dd\pi) = & \frac{15}{2} ABR^6 \frac{e^{-\alpha}}{\alpha} \left\{ \frac{1}{\alpha\beta} \left[1 - \frac{1}{\beta} - \frac{4}{\beta^2} + \frac{12}{\beta^3} + \frac{24}{\beta^4} - \frac{120}{\beta^5} + 24 \frac{e^{-\beta}}{\beta^3} \left(1 + \frac{4}{\beta} + \frac{5}{\beta^2} \right) \right. \right. \\
& + \frac{1}{\alpha} \left(3 - \frac{1}{\beta} - \frac{20}{\beta^2} + \frac{36}{\beta^3} + \frac{168}{\beta^4} - \frac{600}{\beta^5} + 24 \frac{e^{-\beta}}{\beta^3} \left(4 + \frac{18}{\beta} + \frac{25}{\beta^2} \right) \right) \\
& + \frac{3}{\alpha^2} \left(1 - \frac{20}{\beta^2} + \frac{24}{\beta^3} + \frac{216}{\beta^4} - \frac{480}{\beta^5} - 8 \frac{e^{-\beta}}{\beta} \left(1 + \frac{4}{\beta} - \frac{33}{\beta^3} - \frac{60}{\beta^4} \right) \right) \\
& + \frac{24}{\alpha^3\beta} \left(-\frac{5}{\beta} + \frac{3}{\beta^2} + \frac{60}{\beta^3} - \frac{60}{\beta^4} - e^{-\beta} \left(4 + \frac{18}{\beta} + \frac{33}{\beta^2} - \frac{60}{\beta^4} \right) \right) \\
& + \frac{120}{\alpha^4\beta} \left(-\frac{1}{\beta} + \frac{12}{\beta^3} - e^{-\beta} \left(1 + \frac{5}{\beta} + \frac{12}{\beta^2} + \frac{12}{\beta^3} \right) \right) \Bigg] \\
& - \frac{1}{\sigma} \left[\frac{1}{\sigma} \left(1 + \frac{1}{\sigma} - \frac{12}{\sigma^2} - \frac{72}{\sigma^3} - \frac{120}{\sigma^4} + \frac{1440}{\sigma^5} + \frac{10080}{\sigma^6} + \frac{20160}{\sigma^7} - 3e^{-\sigma} \left(3 + \frac{35}{\sigma} \right. \right. \right. \\
& \left. \left. + \frac{228}{\sigma^2} + \frac{1016}{\sigma^3} + \frac{3240}{\sigma^4} + \frac{7200}{\sigma^5} + \frac{10080}{\sigma^6} + \frac{6720}{\sigma^7} \right) \right) \\
& + \frac{1}{\alpha} \left(1 + \frac{2}{\sigma} - \frac{3}{\sigma^2} - \frac{48}{\sigma^3} - \frac{192}{\sigma^4} + \frac{240}{\sigma^5} + \frac{5760}{\sigma^6} + \frac{20160}{\sigma^7} + \frac{20160}{\sigma^8} - \frac{e^{-\sigma}}{\sigma} \left(33 + \frac{329}{\sigma} \right. \right. \\
& \left. \left. + \frac{1848}{\sigma^2} + \frac{7128}{\sigma^3} + \frac{19440}{\sigma^4} + \frac{36000}{\sigma^5} + \frac{40320}{\sigma^6} + \frac{20160}{\sigma^7} \right) \right) \Bigg\}
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{\alpha^2} \left(3 + \frac{2}{\sigma} - \frac{20}{\sigma^2} - \frac{144}{\sigma^3} - \frac{264}{\sigma^4} + \frac{2160}{\sigma^5} + \frac{12960}{\sigma^6} + \frac{20160}{\sigma^7} - 4 \frac{e^{-\sigma}}{\sigma} \left(23 + \frac{193}{\sigma} \right. \right. \\
& \left. \left. + \frac{918}{\sigma^2} + \frac{2934}{\sigma^3} + \frac{6300}{\sigma^4} + \frac{8280}{\sigma^5} + \frac{5040}{\sigma^6} \right) \right) \\
& + \frac{3}{\alpha^3} \left(1 - \frac{20}{\sigma^2} - \frac{96}{\sigma^3} + \frac{72}{\sigma^4} + \frac{1920}{\sigma^5} + \frac{4320}{\sigma^6} - 12 \frac{e^{-\sigma}}{\sigma} \left(5 + \frac{35}{\sigma} + \frac{138}{\sigma^2} + \frac{346}{\sigma^3} \right. \right. \\
& \left. \left. + \frac{520}{\sigma^4} + \frac{360}{\sigma^5} \right) \right) + \frac{24}{\alpha^4 \sigma} \left(-\frac{5}{\sigma} - \frac{12}{\sigma^2} + \frac{60}{\sigma^3} + \frac{240}{\sigma^4} - e^{-\sigma} \left(9 + \frac{53}{\sigma} + \frac{168}{\sigma^2} + \frac{300}{\sigma^3} + \frac{240}{\sigma^4} \right) \right) \\
& \left. + \frac{120}{\alpha^5 \sigma} \left(-\frac{1}{\sigma} + \frac{12}{\sigma^3} - e^{-\sigma} \left(1 + \frac{5}{\sigma} + \frac{12}{\sigma^2} + \frac{12}{\sigma^3} \right) \right) \right\}.
\end{aligned}$$

$$\begin{aligned}
(dd\delta) = & -\frac{15}{2} ABR^6 \frac{e^{-\alpha}}{\alpha} \left\{ \frac{1}{\alpha^2 \beta} \left[1 - \frac{1}{\beta} - \frac{4}{\beta^2} + \frac{12}{\beta^3} + \frac{24}{\beta^4} - \frac{120}{\beta^5} + 24 \frac{e^{-\beta}}{\beta^3} \left(1 + \frac{4}{\beta} + \frac{5}{\beta^2} \right) \right. \right. \\
& + \frac{3}{\alpha} \left(2 - \frac{1}{\beta} - \frac{8}{\beta^2} + \frac{12}{\beta^3} + \frac{48}{\beta^4} - \frac{120}{\beta^5} - 8 \frac{e^{-\beta}}{\beta^2} \left(1 - \frac{9}{\beta^2} - \frac{15}{\beta^3} \right) \right) \\
& + \frac{3}{\alpha^2} \left(5 - \frac{1}{\beta} - \frac{20}{\beta^2} + \frac{12}{\beta^3} + \frac{120}{\beta^4} - \frac{120}{\beta^5} - 8 \frac{e^{-\beta}}{\beta^2} \left(4 + \frac{9}{\beta} - \frac{15}{\beta^3} \right) \right) \\
& \left. + \frac{15}{\alpha^3} \left(1 - \frac{4}{\beta^2} + \frac{24}{\beta^4} - 8 \frac{e^{-\beta}}{\beta^2} \left(1 + \frac{3}{\beta} + \frac{3}{\beta^2} \right) \right) \right] \\
& - \frac{1}{\sigma} \left[\frac{1}{\sigma^2} \left(1 + \frac{3}{\sigma} - \frac{21}{\sigma^2} - \frac{120}{\sigma^3} + \frac{180}{\sigma^4} + \frac{2520}{\sigma^5} + \frac{5040}{\sigma^6} - 3 e^{-\sigma} \left(3 + \frac{33}{\sigma} + \frac{193}{\sigma^2} \right. \right. \right. \\
& \left. \left. + \frac{720}{\sigma^3} + \frac{1740}{\sigma^4} + \frac{2520}{\sigma^5} + \frac{1680}{\sigma^6} \right) \right) \\
& + \frac{1}{\alpha \sigma} \left(1 + \frac{4}{\sigma} - \frac{6}{\sigma^2} - \frac{93}{\sigma^3} - \frac{120}{\sigma^4} + \frac{1260}{\sigma^5} + \frac{5040}{\sigma^6} + \frac{5040}{\sigma^7} - \frac{3 e^{-\sigma}}{\sigma} \left(11 + \frac{101}{\sigma} \right. \right. \\
& \left. \left. + \frac{489}{\sigma^2} + \frac{1500}{\sigma^3} + \frac{2940}{\sigma^4} + \frac{3360}{\sigma^5} + \frac{1680}{\sigma^6} \right) \right) \\
& + \frac{1}{\alpha^2} \left(1 + \frac{5}{\sigma} + \frac{5}{\sigma^2} - \frac{54}{\sigma^3} - \frac{192}{\sigma^4} + \frac{360}{\sigma^5} + \frac{3240}{\sigma^6} + \frac{5040}{\sigma^7} - 4 \frac{e^{-\sigma}}{\sigma^2} \left(23 + \frac{171}{\sigma} \right. \right. \\
& \left. \left. + \frac{657}{\sigma^2} + \frac{1530}{\sigma^3} + \frac{2070}{\sigma^4} + \frac{1260}{\sigma^5} \right) \right) \\
& + \frac{3}{\alpha^3} \left(2 + \frac{4}{\sigma} - \frac{5}{\sigma^2} - \frac{48}{\sigma^3} - \frac{24}{\sigma^4} + \frac{480}{\sigma^5} + \frac{1080}{\sigma^6} - 12 \frac{e^{-\sigma}}{\sigma^2} \left(5 + \frac{29}{\sigma} + \frac{83}{\sigma^2} + \frac{130}{\sigma^3} + \frac{90}{\sigma^4} \right) \right) \\
& + \frac{3}{\alpha^4} \left(5 + \frac{4}{\sigma} - \frac{20}{\sigma^2} - \frac{48}{\sigma^3} + \frac{120}{\sigma^4} + \frac{480}{\sigma^5} - 24 \frac{e^{-\sigma}}{\sigma^2} \left(3 + \frac{13}{\sigma} + \frac{25}{\sigma^2} + \frac{20}{\sigma^3} \right) \right) \\
& \left. + \frac{15}{\alpha^5} \left(1 - \frac{4}{\sigma^2} + \frac{24}{\sigma^4} - 8 \frac{e^{-\sigma}}{\sigma^2} \left(1 + \frac{3}{\sigma} + \frac{3}{\sigma^2} \right) \right) \right\}.
\end{aligned}$$

For $a=b$, that is, $\beta=0$ these expressions reduce to the shorter ones:

$$(dd\sigma) = -\frac{5}{4}A^2R^6\frac{e^{-a}}{a}\left[\frac{11}{15}-\frac{16}{5a}-\frac{18}{5a^2}+\frac{102}{5a^3}+\frac{66}{a^4}+\frac{540}{a^5}+\frac{1884}{a^6}-\frac{16128}{a^7}-\frac{167328}{a^8}-\frac{544320}{a^9}-\frac{544320}{a^{10}}+2\frac{e^{-a}}{a}\left(9+\frac{135}{a}+\frac{1130}{a^2}+\frac{6702}{a^3}+\frac{30372}{a^4}+\frac{105654}{a^5}+\frac{273168}{a^6}+\frac{491904}{a^7}+\frac{544320}{a^8}+\frac{272160}{a^9}\right)\right].$$

$$(dd\pi) = \frac{15}{4}A^2R^6\frac{e^{-a}}{a^2}\left[\frac{11}{15}-\frac{23}{15a}-\frac{66}{5a^2}+\frac{6}{a^3}+\frac{264}{a^4}+\frac{1032}{a^5}-\frac{2016}{a^6}-\frac{35616}{a^7}-\frac{120960}{a^8}-\frac{120960}{a^9}+2\frac{e^{-a}}{a}\left(9+\frac{138}{a}+\frac{1105}{a^2}+\frac{5848}{a^3}+\frac{21996}{a^4}+\frac{59136}{a^5}+\frac{108528}{a^6}+\frac{120960}{a^7}+\frac{60480}{a^8}\right)\right].$$

$$(dd\delta) = -\frac{15}{4}A^2R^6\frac{e^{-a}}{a^3}\left[\frac{11}{15}-\frac{3}{5a}-\frac{21}{a^2}+\frac{6}{a^3}+\frac{510}{a^4}+\frac{672}{a^5}-\frac{7728}{a^6}-\frac{30240}{a^7}-\frac{30240}{a^8}+2\frac{e^{-a}}{a}\left(9+\frac{132}{a}+\frac{974}{a^2}+\frac{4491}{a^3}+\frac{13608}{a^4}+\frac{26544}{a^5}+\frac{30240}{a^6}+\frac{15120}{a^7}\right)\right].$$

The two-centre integrals with $a=b$ are useful in the calculations of the Fletcher type, since Fletcher [2] has made the approximation after which the integrals over the atomic sphere involve only functions with equal exponents. I have followed in numerical calculations this approximation too [4], [5].

Formulae for the case $a\neq b$ are new. They have not yet been used in numerical calculations.

I thank Dr. G. C. Fletcher for his kind correspondence concerning the two-centre integrals.

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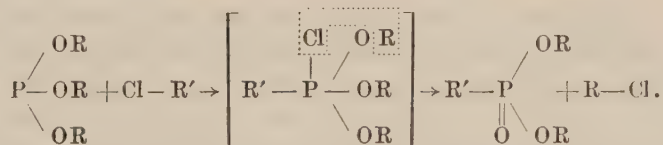
The Action of Alkyl Thiocyanates on Esters of Acids of Trivalent Phosphorus. Synthesis of O,O,S-Trialkyl Thiophosphates

by

J. MICHALSKI and J. WIECZORKOWSKI

Presented by O. ACHMATOWICZ on February 10, 1956

The full esters of trivalent phosphorus acids undergo reaction with organic halides. This transformation is known under the name of Arbuzov's reaction [1] and gives pentavalent phosphorus derivatives, with formation of the carbon-phosphorus bond. It is assumed that Arbuzov's transformation proceeds *via* an intermediate complex, according to the following equation:



Investigation of the reaction between alkyl thiocyanates RSCN and the esters of trivalent phosphorus acids was undertaken as part of a programme concerned with the study of the action of free thiocyanogen and its derivatives on organophosphorus compounds [2]. The investigations recorded in this paper are chiefly concerned with trialkyl phosphites (RO)₃P and dialkyl esters of arylphosphonous acids Ar-P(OR)₂.

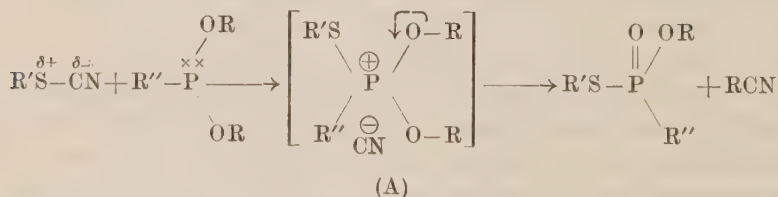
Thiocyanogen can be compared to a halogen: it has been classified as a "pseudohalogen", with an activity placed between bromine and iodine. Free thiocyanogen, like halogens, replaces active hydrogen atoms in some organic compounds and reacts with olefinic and acetylenic linkages, adding to the unsaturated linkage. We have recently established that thiocyanogen, analogically to chlorine [3], reacts with dialkyl phosphites [2]. In some reactions, the behaviour of alkyl thiocyanates is reminiscent of sulphenyl cyanides RS-CN: the sulphur-carbon bond in

the thiocyanate group is disrupted in this reaction, providing an opportunity for introducing the RS-radical into the molecule [4].

If, for instance, alkyl thiocyanates behaved similarly to alkyl halides in the reaction with trialkyl phosphites, this would involve Arbusov's reaction and the formation of dialkyl alkylphosphonates $R'-P(O)(OR)_2$ and of corresponding alkyl thiocyanates. Our experiments have demonstrated that the reaction runs a different course: it gives alkyl cyanides and sulphur containing organophosphorus compounds which we recognized as O, O, S-trialkyl thiophosphates $(R'S)(RO)_2P=O$. Thus, alkyl thiocyanates behave in this reaction in a manner similar to cyano-anhydrides of sulphenic acids.

The reaction between trialkyl phosphites $(RO)_3P$ and alkyl thiocyanates, though distinctly exothermic, calls, nevertheless for an initial heating of the reagents to about 100° . A typical experiment proceeds as follows: trialkyl phosphite and alkyl thiocyanate, in equimolar proportions, are slowly heated in an oil bath to about 100° ; after the vigorous reaction is completed, the mixture is heated for one hour by gradually raising the temperature of the bath to from 160 - 180° , and the evolving alkyl cyanide is distilled off; the O, O, S-trialkyl thiophosphate remaining in the flask is purified by vacuum distillation. The reaction between alkyl thiocyanates and dialkyl esters of arylophosphonous acids $C_6H_5P(OR)_2$ proceeds similarly, but should be conducted under carbon dioxide, since dialkyl arylophosphonite is susceptible to oxidation. Alkyl cyanide and O, O, S-trialkylthiophosphate are both produced in high yield.

The interpretation of the reaction investigated seems obvious. Formation of thiophosphates indicates that alkyl-thiocyanates react with esters of trivalent phosphorus acids under disruption of the carbon-sulphur bond in the thiocyanate group. We propose the following mechanism: in the first stage, there is produced the phosphonium complex (A), which subsequently decomposes, affording alkyl cyanide:



where R'' is an alkoxy or aryl group).

Consequently, the reaction proceeds similarly to the recently described transformation of sulphenyl chlorides with trialkyl phosphites [6] and provides another example of the reaction in which alkyl thiocyanates behave similarly to sulphenyl cyanides.

TABLE

Starting material	Products of reaction	Yield %	B. p. o/mm. Hg	n_D	d_4^{20}	Notes
$(C_2H_5O)_3P$	$(C_2H_5O)_2P-\overset{\overset{O}{\parallel}}{SC_2H_5}$	91	120/17	1.4560 ²⁰	1.1061 ²⁰	[5] B. p. 122.5–123°/20 mm. $n_D^{20}=1.4578$; $d_4^{20}=1.1067$
	C_2H_5CN	90	96	1.3656 ²⁵	—	[7] B. p. 97.1° [9] $n_D^{24}=1.3659$
$(C_2H_5O)_3P$	$(C_2H_5O)_2P-\overset{\overset{O}{\parallel}}{Sn}-C_4H_9$	90	137/15	1.4580 ²⁰	1.0618	B. p. 139°/16 mm; $n_D^{20}=1.4585$
	C_2H_5CN	80	96	1.3658 ²⁵	—	[7] ; [9]
$(C_2H_5O)_3P$	$(C_2H_5O)_2P-\overset{\overset{O}{\parallel}}{SCH_2C_6H_5}$	81	133–4/1	1.5262 ²⁰	1.1540	[5] B. p. 137.5–138°/2.5 mm; $n_D^{20}=1.5258$; $d_4^{20}=1.1569$
	C_2H_5CN	80	96	1.3661 ²⁵	—	[7] ; [9]
$(n-C_4H_9O)_3P$	$(n-C_4H_9O)_2P-\overset{\overset{O}{\parallel}}{SC_2H_5}$	87	152–3/12	1.4548 ²⁰	1.0201	B. p. 156–158°/14 mm.; $n_D^{20}=1.4544$; $d_4^{20}=1.0212$
	$n-C_4H_9CN$	78	139	1.4040 ²⁵	—	[7] B. p. 140.8°; [8] $n_D^{25}=1.3950$
$C_6H_5P(OC_2H_5)_2$	$C_6H_5P(\overset{\overset{O}{\parallel}}{OC_2H_5})_2 (SC_2H_5)$	83	96–7/0.02	1.5410 ²⁰	1.1395	
	C_2H_5CN	75	96	1.3652 ²⁵	—	[7] ; [9]

The notes quote physical constants of corresponding compounds described in literature or obtained by known methods.

The reaction described constitutes a new method for the preparation of O, O, S-trialkyl thiophosphates, O, S-dialkyl arylthiophosphonates, and alkyl cyanides.

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Heteroazeotropic Binary Systems.

I. Influence of Temperature on the Equilibrium Pressure and on the Vapour Composition

by

J. STECKI

Presented by W. ŚWIEȚOSŁAWSKI on February 27, 1956

1. Introductory remarks

The changes in the composition of the homoazeotrope in a given system under the conditions of varying temperature and pressure may be predicted on the basis of the well known Vrevski rule [4]. In this paper a similar rule is derived, for all systems in which vapour coexists with two condensed phases, liquid or solid. The results and considerations are directly applicable to the heteroazeotropic systems [1], since the composition of the heteroazeotrope may be considered as that of vapour coexisting with two liquid phases. Classical thermodynamics of phase equilibria is used [2]. All symbols introduced in this paper may be conventionally applied in thermodynamics. Most of them are identical with those found in "Chemical Thermodynamics" of I. Prigogine and R. Defay [2].

2. Equilibrium conditions

Let us consider a binary system composed of three phases in the state of equilibrium. The chemical potential of the given component, 1 or 2, must be expressed by equal values in all three phases, symbolised by the indexes α , β , and v . We have, therefore,

$$(1) \quad \mu_i^k = \mu_i^l \quad (i=1,2; k, l=\alpha, \beta, v; k \neq l),$$

and

$$(2) \quad \delta\mu_i^k = \delta\mu_i^l \quad (k, l=\alpha, \beta, v; i=1,2; k \neq l).$$

Because

$$\delta\mu_1^q = -S_1^q \delta T + V_1^q \delta p - x^q g_{22}^q \delta x^q,$$

$$\delta\mu_2^q = -S_2^q \delta T + V_2^q \delta p + (1 - x^q) g_{22}^q \delta x^q,$$

where S_i^q is the partial molar entropy of component "i" in the phase "q", V_i^q the partial molar volume of component "i" in the phase "q", and x^q stands for the mole fraction of the component "2"; g_{22}^q is equal to $\left(\frac{\partial^2 G}{\partial x^2}\right)_{P,T}^{(q)}$, where $G^{(q)} = H^{(q)} - TS^{(q)}$ is the mean molar Gibbs free energy of phase "q"; after rearranging, on the basis of (2), we obtain the following set of equations:

$$(3a) \quad (V_1^a - V_1^\beta) \frac{\delta p}{\delta T} - x^a g_{22}^a \frac{\delta x^a}{\delta T} + x^\beta g_{22}^\beta \frac{\delta x^\beta}{\delta T} = S_1^a - S_1^\beta,$$

$$(3b) \quad (V_2^a - V_2^\beta) \frac{\delta p}{\delta T} + (1 - x^a) g_{22}^a \frac{\delta x^a}{\delta T} - (1 - x^\beta) g_{22}^\beta \frac{\delta x^\beta}{\delta T} = S_2^a - S_2^\beta,$$

$$(3c) \quad (V_1^v - V_1^\beta) \frac{\delta p}{\delta T} + x^a g_{22}^a \frac{\delta x^a}{\delta T} - y g_{22}^v \frac{\delta y}{\delta T} = S_1^v - S_1^\beta,$$

$$(3d) \quad (V_2^v - V_2^\beta) \frac{\delta p}{\delta T} - (1 - x^a) g_{22}^a \frac{\delta x^a}{\delta T} + (1 - y) g_{22}^v \frac{\delta y}{\delta T} = S^v - S_2^\beta,$$

$$(3e) \quad (V_1^v - V_1^\beta) \frac{\delta p}{\delta T} + x^\beta g_{22}^\beta \frac{\delta x^\beta}{\delta T} - y g_{22}^v \frac{\delta y}{\delta T} = S_1^v - S_1^\beta,$$

$$(3f) \quad (V_2^v - V_2^\beta) \frac{\delta p}{\delta T} - (1 - x^\beta) g_{22}^\beta \frac{\delta x^\beta}{\delta T} + (1 - y) g_{22}^v \frac{\delta y}{\delta T} = S^v - S_2^\beta.$$

Equations (3) express the variations of the pressure δp , of the temperature δT , of the three concentrations δx^a , δx^β , δy ($y \equiv x^v$), caused by the heat and volume effects. Of these equations four only may be considered as, if properly chosen, linearly independent. Solving equations *a*, *b*, *c*, *d* we obtain

$$(4) \quad \frac{\delta p}{\delta T} = \frac{(x^a - x^\beta) S_a^v + (y - x^a) S_a^\beta}{(x^a - x^\beta) V_a^v + (y - x^a) V_a^\beta},$$

$$(5) \quad g_{22}^v \frac{\delta y}{\delta T} = \frac{S_a^v V_a^\beta - V_a^v S_a^\beta + (x^a - x^\beta) [(S_2^v - S_2^\beta)(V_1^v - V_1^\beta) - (S_1^v - S_1^\beta)(V_2^v - V_2^\beta)]}{(x^a - x^\beta) V_a^v + (y - x^a) V_a^\beta},$$

$$(6) \quad g_{22}^a \frac{\delta x^a}{\delta T} = \frac{S_a^\beta V_a^v - V_a^\beta S_a^v}{(x^a - x^\beta) V_a^v + (y - x^a) V_a^\beta},$$

$$(7) \quad g_{22}^\beta \frac{\delta x^\beta}{\delta T} = \frac{V_a^\beta S_a^v - S_a^\beta V_a^v + (x^a - y) [(S_1^a - S_1^\beta)(V_2^a - V_2^\beta) - (V_1^a - V_1^\beta)(S_2^a - S_2^\beta)]}{(x^a - x^\beta) V_a^v + (y - x^a) V_a^\beta}.$$

Other forms of the algebraic solution can be obtained by cyclic permutation of the indexes of the phases α , β , v . For example,

$$(8) \quad \frac{\delta p}{\delta T} = \frac{(x^\beta - y)S_\beta^\alpha + (x^\alpha - x^\beta)S_\beta^v}{(x^\beta - y)V_\beta^\alpha + (x^\alpha - x^\beta)V_\beta^v} = \frac{(y - x^\alpha)S_v^\beta + (x^\beta - y)S_v^\alpha}{(y - x^\alpha)V_v^\beta + (x^\beta - y)V_v^\alpha},$$

$$(9) \quad g_{22}^v \frac{\delta y}{\delta T} = \frac{S_v^\alpha V_v^\beta - V_v^\alpha S_v^\beta}{(y - x^\alpha)V_v^\beta + (x^\beta - y)V_v^\alpha}.$$

S_β^α is the differential change of the total molar entropy during the phase transformation $\beta \rightarrow \alpha$, and is equal to $(1 - x^\alpha)(S_1^\alpha - S_1^\beta) + x^\alpha(S_2^\alpha - S_2^\beta)$. Similarly V_α^v is the differential volume effect, equal to $(1 - y)(V_1^v - V_1^\alpha) + y(V_2^v - V_2^\alpha)$.

3. Approximate equations

The results thus derived are entirely general and may be applied to any three phase binary system. If "v" is the vapour phase, and "a", "b", the two liquid or other condensed phases, we may at ordinary pressures disregard the volume of the condensed phases and assume that the vapour behaves as a perfect gas. In that case

$$(10) \quad V_1^v = V_2^v = RT/p; \quad g_{22}^v = RT/y(1 - y).$$

Hence, we obtain the following approximate equations:

$$(11) \quad RT \frac{\delta \log p}{\delta T} = S_\beta^v + \frac{x^\beta - y}{x^\alpha - x^\beta} S_\beta^\alpha = S_\alpha^v + \frac{y - x^\alpha}{x^\alpha - x^\beta} S_\alpha^\beta = \frac{(y - x^\alpha)S_v^\beta + (x^\beta - y)S_v^\alpha}{x^\alpha - x^\beta},$$

$$(12) \quad g_{22}^v \frac{\delta y}{\delta T} = (S_2^v - S_2^\alpha) - (S_1^v - S_1^\alpha) + \frac{S_\alpha^\beta}{x^\alpha - x^\beta} = (S_2^v - S_2^\beta) - (S_1^v - S_1^\beta) + \frac{-S_\beta^\alpha}{x^\alpha - x^\beta} = S_2^v - S_1^v + \frac{S(x^\beta) - S(x^\alpha)}{x^\alpha - x^\beta}.$$

and the well known relations [2]:

$$(13) \quad g_{22}^a \frac{\delta x^\alpha}{\delta T} = S_\alpha^\beta / (x^\alpha - x^\beta),$$

$$(14) \quad g_{22}^\beta \frac{\delta x^\beta}{\delta T} = -S_\beta^\alpha / (x^\alpha - x^\beta).$$

Derivatives $\delta p / \delta T$ and $\delta y / \delta T$ may also be expressed as follows:

$$(15) \quad RT \frac{\delta \log p}{\delta T} = S^{(v)} - \frac{(x^\alpha - y)S^{(\beta)} + (y - x^\beta)S^{(\alpha)}}{x^\alpha - x^\beta},$$

$$(16) \quad \frac{RT}{y(1-y)} \cdot \frac{\delta y}{\delta T} = \frac{S_v^\beta - S_v^\alpha}{x^\alpha - x^\beta},$$

$$(16a) \quad \frac{RT^2}{y(1-y)} \cdot \frac{\delta y}{\delta T} = \frac{H_v^\beta - H_v^\alpha}{x^\alpha - x^\beta}.$$

Because of the relations of the type $H_i^\alpha - H_i^\beta = T(S_i^\alpha - S_i^\beta)$, all the entropy effects in the equations above derived may be replaced by the respective heat effects (enthalpy effects), multiplied by T .

4. Discussion

Equations (11), (12), (15), (16) express the influence of the temperature on the equilibrium pressure and on the vapour composition in the three-phase system. In a heteroazeotropic system, this may be called the "composition of the heteroazeotrope". The equations last referred to may be interpreted as differential equations of a line, formed by points representing the considered three-phase system in a P , T , y diagram.

Attention should be given to the symmetrical form of the right side of equation (15). The first term $S^{(v)}$ is simply the molar total entropy of the vapour phase; the second may be interpreted as the mean molar entropy of a liquid system having the same composition as the vapour phase, y , and being built up by the two saturated liquid solutions, mixed in fixed proportions: $x^\alpha - y$ moles of phase β , $y - x^\beta$ moles of phase α . This interpretation is quite correct when $x^\alpha > y > x^\beta$, or $x^\alpha < y < x^\beta$. In these cases, however, where $y > x^\alpha$, x^β , or where $y < x^\alpha$, x^β , it becomes somewhat fictitious. For comparison we quote the analogous equation, fulfilled in the case of a homoazeotrope:

$$(17) \quad RT \frac{\delta \log p}{\delta T} = S^{(v)} - S^{(L)},$$

where $S^{(L)}$ is the molar total entropy of the liquid phase. The result expressed by equation (15) may be anticipated on the basis of the known properties of what is called by some authors "indifferent states", because we have here an example of an "indifferent system" [2].

Equation (16) expresses the influence of the temperature on the vapour composition in terms of quantities H_v^α and H_v^β , or S_v^α and S_v^β . Taking " α " as the more dilute phase in component " v " we conclude that:

$$(18) \quad \delta y / \delta T \geq 0, \quad \text{if} \quad |S_v^\alpha| \geq |S_v^\beta|, \quad \text{because} \quad x^\alpha - x^\beta > 0;$$

$$(19) \quad \delta y / \delta T \geq 0, \quad \text{if} \quad |H_v^\alpha| \geq |H_v^\beta|,$$

remembering that heat and entropy effects are negative.

Let us consider the quantities H_v^a and H_v^b , appearing in equations (16)-(19). H_v^a equals $(1-x^a)(H_1^a-H_1^v)+x^a(H_2^a-H_2^v)$ (see 2). According to this definition, it follows that H_v is, by taking the required amounts of the components "1" and "2" from the vapour phase, the enthalpy change in the course of the formation, at constant T and p , of one mole of phase a . The similar quantity H_a^v is the enthalpy effect evolved in the course of the formation of one mole of vapour phase by evaporation of the coexisting phase a , this being taken in order to prevent the changes in composition of both phases in a very large amount. According to generally accepted conventions, H_a^v may be called the total molar differential heat of evaporation of the solution " a ", and for the quantity H_v^a the term of the *total molar differential heat of condensation* of the phase " a " may be introduced. Unfortunately, it is not possible in our case to carry out the required physical process, because the condensation of the vapour leads to simultaneous appearance of both liquid phases. The latter term is retained, however, for simplification purposes only. H_v^a (or H_v^b) may be interpreted as a limiting value, to which the real differential heats of condensation of unsaturated solutions tend, the corresponding compositions approaching to the saturated one (x^a or x^b). It is evident that the differential heats of condensation are always negative quantities.

On the basis of equation (19) the changes in the vapour composition may be predicted as follows:

The increase in temperature (and pressure) is associated with the increase in the vapour phase of the mole fraction of that component, the molar concentration of which is larger in the liquid phase, characterised by a greater absolute value of the differential heat of condensation.

This rule is equally applicable for the prediction of the changes in composition of a heteroazeotrope, as in that of vapour coexisting with two liquid phases, in the case of a heteroazeotrope or homoazeotrope outside the miscibility gap.

It remains to consider the limits of applicability of the conclusions presented in this paper. The equations (4)-(9) in 2, as well as any other algebraic solution of the set (3), are applicable to any three-phase binary system. On the contrary, the approximate equations (11)-(16a), as well as the rule just formulated, are limited to the cases in which the vapour may be considered as a perfect gas, and the volume of the condensed phases may be disregarded. It is probable that the qualitative rule will be fulfilled far beyond the limits of quantitative applicability of equation (16), on which it is based. It should be emphasised that the two condensed phases may be liquid or solid. Moreover, the shape of the miscibility curve exerts its influence indirectly only. For this reason, the equations mentioned above are valid in all cases — whether there

exists an upper or a lower critical solubility temperature, or even if such does not exist at all.

I wish to express my thanks to Professor W. Świątosławski for a suggestion which initiated this work as well as for his kind interest and advice.

Summary

1. On the basis of thermodynamic considerations, several differential relations between the compositions of the phases, the pressure and the temperature are derived in the case of three-phase binary systems.

2. These relations are simplified in the case of vapour and two condensed phase systems.

3. The rule is formulated, according to which, in a three-phase system, the increase in temperature (and pressure) is associated with the increase in the vapour phase of the mole fraction of that component the molar concentration of which is larger in the liquid phase, characterised by a larger absolute value of the differential heat of condensation.

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Heteroazeotropic Binary Systems.

II. Influence of the Pressure and of the Heats of Mixing

by

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Presented by W. ŚWIEȚOSŁAWSKI on February 27, 1956

1. Introductory remarks

In the previous paper [1], there was derived a set of differential equations expressing the equilibrium conditions of the three-phase binary liquid-liquid-vapour systems. These equations expressed the influence of the temperature on the equilibrium pressure and on the vapour composition, in some cases in exact, and in others in approximate, form. Here, an attempt is made to derive similar equations, expressing the influence of pressure on the boiling temperature and the vapour composition in these systems.

2. Influence of pressure

Because the systems considered are monovariant, the change of variables may be expressed in a simple manner:

$$(1) \quad \frac{\delta X}{\delta p} = \frac{\delta X}{\delta T} / \frac{\delta p}{\delta T},$$

where X may be any variable, T is the absolute temperature and P the total equilibrium pressure of the system. When using four equations discussed in 2 of the previous paper [1], namely

$$(I.3a) \quad (V_1^a - V_1^\beta) \frac{\delta p}{\delta T} - x^a g_{22}^a \frac{\delta x^a}{\delta T} + x^\beta g_{22}^\beta \frac{\delta x^\beta}{\delta T} = S_1^a - S_1^\beta,$$

$$(I.3b) \quad (V_2^a - V_2^\beta) \frac{\delta p}{\delta T} + (1 - x^a) g_{22}^a \frac{\delta x^a}{\delta T} - (1 - x^\beta) g_{22}^\beta \frac{\delta x^\beta}{\delta T} = S_2^a - S_2^\beta,$$

$$(I.3c) \quad (V_1^v - V_1^a) \frac{\delta p}{\delta T} + x^a g_{22}^a \frac{\delta x^a}{\delta T} - y g_{22}^v \frac{\delta y}{\delta T} = S_1^v - S_1^a,$$

$$(I.3d) \quad (V_2^v - V_2^a) \frac{\delta p}{\delta T} - (1 - x^a) g_{22}^a \frac{\delta x^a}{\delta T} + (1 - y) g_{22}^v \frac{\delta y}{\delta T} = S_2^v - S_2^a,$$

we obtain the following relations *)

$$(2) \quad \frac{\delta T}{\delta p} = \frac{(x^a - x^\beta) V_a^v + (y - x^a) V_a^\beta}{(x^a - x^\beta) S_a^v + (y - x^a) S_a^\beta},$$

$$(3) \quad g_{22}^v \frac{\delta y}{\delta p} = \frac{S_v^a V_a^\beta - S_a^\beta V_v^a + (x^a - x^\beta) [(S_2^v - S_2^a) (V_1^v - V_1^a) - (V_2^v - V_2^a) (S_1^v - S_1^a)]}{(x^a - x^\beta) S_a^v + (y - x^a) S_a^\beta},$$

$$(4) \quad g_{22}^a \frac{\delta x^a}{\delta p} = \frac{S_a^\beta V_a^v - V_a^\beta S_a^v}{(x^a - x^\beta) S_a^v + (y - x^a) S_a^\beta},$$

$$(5) \quad g_{22}^\beta \frac{\delta x^\beta}{\delta p} = \frac{V_\beta^a S_a^v - S_\beta^a V_a^v + (x^a - y) [(S_1^a - S_1^\beta) (V_2^a - V_2^\beta) - (V_1^a - V_1^\beta) (S_2^a - S_2^\beta)]}{(x^a - x^\beta) S_a^v + (y - x^a) S_a^\beta}.$$

Assuming that the vapour phase behaves as the perfect gas, and that its molar volume is overwhelmingly greater than the molar volumes of the condensed phases, we obtain the following relations:

$$(6) \quad \frac{\delta T}{\delta p} = \frac{RT}{p} \cdot \frac{x^a - x^\beta}{(x^\beta - y) S_\beta^a + (x^a - x^\beta) S_\beta^v},$$

$$(7) \quad \frac{p}{y(1-y)} \cdot \frac{\delta y}{\delta p} = \frac{S_a^\beta + (x^a - x^\beta) \{ (S_2^v - S_2^a) - (S_1^v - S_1^a) \}}{(x^a - x^\beta) S_a^v + (y - x^a) S_a^\beta},$$

or in more symmetrical form

$$(8) \quad \frac{\delta T}{\delta p} = \frac{RT}{p} \cdot \frac{x^a - x^\beta}{(y - x^a) S_v^\beta + (x^\beta - y) S_v^a},$$

$$(9) \quad \frac{P}{y(1-y)} \frac{\delta y}{\delta p} = \frac{S_v^a - S_v^\beta}{(y - x^a) S_v^\beta + (x^\beta - y) S_v^a}.$$

Equations (6), (7), (8), (9), are because of the assumptions introduced and mentioned above, valid under suitably low pressures only. The symbols are identical with those used in (1). x^v represents the mole fraction of the component "2" in the phase " φ ". $X_{\varphi_1}^{\varphi_2}$ is the molar differential effect of the variable X , if one mole of the phase " φ_2 " is formed from the coexisting phase " φ_1 ", provided that the compositions remain unchanged. g_{22}^v is second partial derivative of the Gibbs free energy of the

*) These equations may be applied to any three-phase binary system.

phase " φ " with respect to composition x^φ . It may be concluded that in order to obtain the (exact) derivative with respect to pressure, it suffices to replace, in the denominator of the corresponding derivative with respect to temperature, all the differential volume effects by the corresponding entropy effects. We see also that the derivatives with respect to temperature are simpler and easier to handle.

3. Heats of mixing

The equations under consideration deal with the differential heat effects. For example, we have to use the differential heats of evaporation from the solution, which are not readily available quantities. Therefore it is convenient to express our results in the way which make it possible to operate with the heats of mixing which characterize the solutions examined. The enthalpy of mixing is defined as the difference between the enthalpy of the given solution H , and that of a hypothetical ideal solution, formed by the same components:

$$\Delta^m H = H - (1-x)H_1^0 - xH_2^0 = (1-x)\Delta^m H_1 + x\Delta^m H_2.$$

The partial molar heats of mixing $\Delta^m H_i$ ($i=1,2$) are defined by the equations $\Delta^m H_i = H_i - H_i^0$, ($i=1,2$) in which H_i is the partial molar enthalpy of component " i " in the solution, and H_i^0 that of a pure substance " i ". Thus, the difference between the partial molar enthalpy of the component " i " in the vapour, and that in the liquid phase, may be expressed as the difference between the heat of evaporation of the pure component " i ", $\Delta^{\text{vap}} H_i^0$, and the partial molar heat of mixing at its concentration in liquid saturated solution, assuming again that the gaseous phase behaves in an ideal manner. Thus, we obtain from the approximate equations (7) or (9) the following:

$$(10) \quad \frac{p}{y(1-y)} \frac{\delta y}{\delta p} = \frac{(x^\alpha - x^\beta)(\Delta^{\text{vap}} H_2^0 - \Delta^{\text{vap}} H_1^0) + \Delta^m H(x^\beta) - \Delta^m H(x^\alpha)}{(x^\alpha - x^\beta)[(1-y)\Delta^{\text{vap}} H_1^0 + y\Delta^{\text{vap}} H_2^0] + (x^\beta - y)\Delta^m H(x^\alpha) + (y - x^\alpha)\Delta^m H(x^\beta)},$$

and from the equation (11)

$$(I.11) \quad RT \frac{\delta \log p}{\delta T} = \frac{(y - x^\alpha) S_v^\beta + (x^\beta - y) S_v^\alpha}{x^\alpha - x^\beta},$$

or (15)

$$(I.15) \quad RT \frac{\delta \log p}{\delta T} = S^{(v)} - \frac{(x^\alpha - y) S^{(\beta)} + (y - x^\alpha) S^{(\alpha)}}{x^\alpha - x^\beta}$$

of [1] we have:

$$(11) \quad RT^2 \frac{\delta \log p}{\delta T} = (1-y) \Delta^{\text{vap}} H_1^0 + y \Delta^{\text{vap}} H_2^0 + \frac{(y-x^\alpha) \Delta^m H(x^\beta) + (x^\beta - y) \Delta^m H(x_\beta)}{x^\alpha - x^\beta};$$

finally, from equation (16)

$$(I.16) \quad \frac{RT}{y(1-y)} \frac{\delta y}{\delta T} = \frac{S_v^\beta - S_v^\alpha}{x^\alpha - x^\beta}$$

of [1] we obtain:

$$(12) \quad \frac{RT^2}{y(1-y)} \frac{\delta y}{\delta T} = \Delta^{\text{vap}} H_2^0 - \Delta^{\text{vap}} H_1^0 - \frac{\Delta^m H(x^\alpha) - \Delta^m H(x^\beta)}{x^\alpha - x^\beta}.$$

Equation (12) may be interpreted as follows. The heat of mixing is usually much smaller than the evaporation enthalpy. It may be shown that the quotient $\Delta^m H(x^\alpha) = \Delta^m H(x^\beta)/(x^\alpha - x^\beta)$ approaches to zero if the critical mixing conditions are attained. Hence, its value remains always finite. It follows that in most cases, especially if a qualitative prediction has to be made, the term containing the heats of mixing may be disregarded. With that approximation it follows that:

$$\delta y / \delta T \geq 0, \quad \text{if} \quad \Delta^{\text{vap}} H_2^0 \geq \Delta^{\text{vap}} H_1^0.$$

Therefore an increase in temperature leads to an enrichment of the vapour phase in that component which is characterised by a higher heat of evaporation. This result is identical with the simplified Vrevski's rule [4], dealing with the positive homoazeotropes.

This rule has been qualitatively proved by experimental data. In the case of the water-isobutanol system (3), it is seen that the agreement is only qualitative; the change in heteroazeotropic composition per 1°C., found experimentally, is much smaller than that anticipated on the basis of the heats of evaporation. On the other hand, the more general equation (12) or (I.16), (I) may be used in calculations, apparently with success only in cases where the required experimental data are available.

In addition, it should be emphasized that the influence of temperature and pressure on the composition of homoazeotropes (and not heteroazeotropes) has been examined by a number of authors [2], [4], [5].

Summary

1. The equations derived in the previous paper [1] are modified by introducing the pressure as an independent variable.

2. The role of the mixing enthalpy is emphasized.

3. It is proved that the approximate rule, formulated long ago for the positive homoazeotropes and based on the difference in evaporation enthalpies of the pure components may also be used as the first approximation in systems characterized by a partial mutual solubility of the components in liquid state.

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Series of Binary Azeotropic Systems Characterised by Asymmetrical Azeotropic Ranges

by

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1. Introductory remarks

In the previous papers [1], [2], [3] basing on the value of the azeotropic range and its upper and lower portions as defined by Świętosławski [4], we developed the relations between the azeotropic depressions $\delta_A = T_A - T_{Az}$, $\delta_{H_i} = T_{H_i} - T_{Az}$ and the composition of the azeotrope. We expressed them in the following way:

$$(1a) \quad \delta_A = Z_d x_{H_i}^2,$$

$$(1b) \quad \delta_{H_i} = Z_g x_A^2,$$

where Z_g , Z_d are the respective upper and lower portions of the azeotropic range and x_{H_i} , x_A — the mole fractions of the components in the azeotrope AH_i .

According to the previous considerations [1], [2], the values Z_g and Z_d are defined by the relations

$$(2a) \quad Z_d = \frac{A_{AH}}{\Delta S_A},$$

$$(2b) \quad Z_g = \frac{A_{AH}}{\Delta S_H},$$

A_{AH} being a parameter characterising the regular solutions, which remains constant for the whole series of binary azeotropic systems (AH_i); ΔS_A and ΔS_H represent the evaporation entropies at the boiling temperature of the component A and the homologues H respectively.

When deriving further relations, following from equations (1a) and (1b), and relating the azeotropic depression to the boiling temperature differences of the components, as well as the azeotropic composition to

the value of these differences, we have introduced another simplification, namely, we have assumed that not only the representatives of a given series of homologues (H), but also the azeotropic agent A are characterised by equal evaporation entropies ($\Delta S_A = \Delta S_H$).

In this paper we give up this simplification, and we assume that the evaporation entropy of agent A and those of the representatives of the series (H) are not equal to one another. For this reason we have to modify the relations mentioned above between the azeotropic depression, the boiling temperature differences of the components, and the azeotropic composition of the azeotropes (ΔH_i) under examination.

It must be added, that in the case when $\Delta S_A = \Delta S_H$, the lower portion of the range equals the upper one: $Z_d = Z_g$. Hence, the whole range is symmetrical with respect to the boiling temperature of agent A . If ΔS_A is not equal to ΔS_H , values Z_d and Z_g are also not equal. Their ratio, according to (2), is now expressed by the relation:

$$(3) \quad \frac{Z_d}{Z_g} = \frac{\Delta S_H}{\Delta S_A}.$$

Consequently, in conformity with the value of the entropy ratio, the azeotropic range: $Z = Z_d + Z_g$ is characterised by a certain asymmetry.

2. Relations between the azeotropic depressions

Determining x_A and x_{H_i} from the respective equations (1a) and (1b), and inserting them into the relation $x_A + x_{H_i} = 1$, we obtain

$$(4) \quad \sqrt{\frac{\delta_A}{Z_d}} + \sqrt{\frac{\delta_{H_i}}{Z_g}} = 1.$$

It is the basic relation between the temperature azeotropic parameters, i. e. those, the values of which depend only upon the boiling temperature of pure components and that of the azeotropic mixture. Equation (4) does not contain any parameter combined with the azeotropic composition. With the help of equation (3), the values of Z_d and Z_g may be calculated from equation (4) as follows:

$$(5) \quad Z_d = \left(\sqrt{\delta_A} + \sqrt{\delta_{H_i}} \sqrt{\frac{\Delta S_H}{\Delta S_A}} \right)^2,$$

$$(6) \quad Z_g = \left(\sqrt{\delta_A} \sqrt{\frac{\Delta S_A}{\Delta S_H}} + \sqrt{\delta_{H_i}} \right)^2.$$

It should be emphasised that equations (5) and (6) show a satisfactory agreement with experimental data even in those cases, where the azeotropes deviate considerably from the properties of regular solutions. This fact, illustrated below by some examples, determines the availability of

the latter for calculating the values of the azeotropic ranges. In fact, it is easy to see that it suffices to know the boiling temperature of one of the azeotropes (ΔH_i) of a given series, if the boiling temperatures and the evaporation entropies of the pure components are known. If $T_A = T_{H_i}$, δ_A must be equal to δ_{H_i} . This means that the relations (5) and (6) transform themselves into

$$(7) \quad Z_d = \left(1 + \sqrt{\frac{\Delta S_H}{\Delta S_A}}\right)^2 \delta, \quad Z_g = \left(1 + \sqrt{\frac{\Delta S_A}{\Delta S_H}}\right)^2 \delta.$$

In the case of equal evaporation entropies, we get a very simple expression:

$$(8) \quad Z_d = Z_g = 4\delta.$$

This result may lead to an approximatively established rule: If the boiling temperatures of the components are very close to each other, the azeotropic range Z equals the eightfold value of the azeotropic depression.

3. Relation between the azeotropic depression and the difference in boiling temperatures of the components

Using the parameters $\Delta_A = T_A - T_{H_i}$; $\Delta_{H_i} = T_{H_i} - T_A$ we obtain a modification of relation (4). Substituting δ_A by $\delta_{H_i} - \Delta_{H_i}$, and δ_{H_i} by $\delta_A - \Delta_A$ in equation (4) we obtain:

$$(9a) \quad \sqrt{\frac{\delta_{H_i} - \Delta_{H_i}}{Z_d}} + \sqrt{\frac{\delta_{H_i}}{Z_g}} = 1;$$

$$(9b) \quad \sqrt{\frac{\delta_A}{Z_d}} + \sqrt{\frac{\delta_A - \Delta_A}{Z_g}} = 1.$$

Introducing relation (3), we get another two equations:

$$(10a) \quad \Delta_{H_i} = -Z_d + 2\sqrt{Z_d} \sqrt{\delta_{H_i}} \sqrt{\frac{\Delta S_H}{\Delta S_A}} + \delta_{H_i} \left(1 - \frac{\Delta S_H}{\Delta S_A}\right),$$

$$(10b) \quad \Delta_A = -Z_g + 2\sqrt{Z_g} \sqrt{\delta_A} \sqrt{\frac{\Delta S_A}{\Delta S_H}} + \delta_A \left(1 - \frac{\Delta S_A}{\Delta S_H}\right).$$

Equations (10a) and (10b) fulfill the limit conditions. In fact, if $\delta_{H_i} = 0$ — then $\Delta_{H_i} = -Z_d$, and if $\delta_A = 0$ — then $\Delta_A = -Z_g$. Under the conditions $\delta_{H_i} = Z_g$ and $\delta_A = Z_d$, the respective boiling temperature differences Δ_{H_i} and Δ_A are equal to the corresponding values of the portions of the azeotropic range Z_g and Z_d . The assumption, however, that the entropies of evaporation are equal to one another is associated with a simplification of equations (10a) and (10b), so that they transform themselves into those derived for the series of azeotropes characterised by sym-

metrical azeotropic ranges [1], [2]:

$$(11a) \quad \Delta_{H_i} = -\frac{1}{2}Z + \sqrt{2Z} \sqrt{\delta_{H_i}},$$

$$(11b) \quad \Delta_A = -\frac{1}{2}Z + \sqrt{2Z} \sqrt{\delta_A}.$$

It should be stressed that, if the evaporation entropies are slightly different from one another, the errors caused by simplification of the equation (10a) and (10b) will be small. For this reason the calculations based upon the equations (11a) and (11b) may be applied with satisfactory results.

4. Composition of the azeotropes (ΔH_i) as the function of the boiling temperatures difference of the components

Subtracting equations (1a) from (1b) and substituting the difference $\delta_A - \delta_{H_i}$ by Δ_A , we obtain

$$(12) \quad \Delta_A = Z_d x_{H_i}^2 - Z_g x_A^2.$$

After some transformations and with the aid of equation (3), the relation (12) may be written as follows:

$$(13) \quad x_{H_i} = \frac{\sqrt{\Delta S_A}}{\sqrt{\Delta S_H} + \sqrt{\Delta S_A}} + \frac{\Delta_A}{Z_d \left(x_{H_i} + \sqrt{\frac{\Delta S_A}{\Delta S_H} x_A} \right) \left(1 + \sqrt{\frac{\Delta S_A}{\Delta S_H}} \right)}$$

or

$$(14) \quad x_{H_i} = \frac{1}{2} + \frac{\Delta_A}{2Z_g} + \frac{x_{H_i}^2}{2} \left(1 - \frac{\Delta S_H}{\Delta S_A} \right).$$

It has been emphasised that both these equations are equivalent. They are written differently in order to simplify the discussion on how the composition of azeotrope (ΔH_i) depends upon the boiling temperatures difference of the components. If the boiling temperatures of the components are equal, that is $\Delta_A = 0$, then, according to equation (13), the composition of the azeotrope would be determined by the relation

$$(15) \quad x_{H_i} = \frac{\sqrt{\Delta S_A}}{\sqrt{\Delta S_H} + \sqrt{\Delta S_A}}.$$

In this case the azeotropic composition is not equal to 0.5, as in the systems characterised by symmetrical azeotropic ranges. If $\Delta S_A > \Delta S_H$, then $x_{H_i} > 0.5$.

Let us determine the conditions under which the boiling temperatures difference of the components corresponds to the composition of the azeotrope $x_{H_i} = x_A = 0.5$. Substituting $x_{H_i} = 0.5$ in equation (14) and introducing the ratio of the azeotropic ranges instead of that of entropies, we find

$$(16) \quad \Delta_A = \frac{1}{4}(Z_d - Z_g).$$

Consequently, it follows that, if $\Delta S_A > S_H$ i. e. $Z_g > Z_d$, the boiling temperature T_{H_i} should be higher than T_A .

5. Experimental verification of the equations

In order to show the applicability of the equations mentioned above, a number of examples for several azeotropic series is given in Table I. The values of the upper and the lower portion of the azeotropic range were calculated on the basis of experimentally known azeotropic data. Examples have been chosen in which the alcohols and the esters form azeotropes with aliphatic, aromatic and naphthenic hydrocarbons. They are characterised by considerable differences in evaporation entropy of the components, and they show large deviation from the regular solution properties. This is especially evident for the azeotropes formed by alcohols. The columns in Table I represent: 1 — the number of the series; 2 — the number of the homologue; 3 — the name of the azeotropic agent and the respective homologue; 4 — the boiling temperature of the components (t_A or t_{H_i}); 5 — their evaporation entropies ΔS ; 6 — the boiling temperatures of the respective azeotropes t_{Az} ; 7 — the value of the lower portion of the azeotropic range Z_d , calculated according to equation (5), 8 — the value of the upper portion of the azeotropic range Z_g calculated according to equation (6). In column 9 the values of $\frac{1}{2}Z$ are given. They are calculated by means of equations (11a) or (11b), under the assumption, that the azeotropic range is symmetrical. In the column 10 the deviations of the value of the lower portions Z_d of the azeotropic range from the mean value Z_m are given. The latter values are calculated without taking into consideration the most deviating values of Z_d . Lecat's [5] azeotropic data have been used. The evaporation entropy have been taken from Partington's [6] monograph and Rossini's tables [7].

In spite of the fact, that the systems show large deviations from the properties of regular solutions, the values found for Z_d are practically constant. The existence of these deviations may be deduced from the fact that equations (1a) or (1b) are not fulfilled [3]. It is seen therefore, that some series of azeotropic systems may fulfill equations (5) and (6), while showing comparatively great deviations from equation (1a) and (1b). It is considered to be associated with the absence of concentration parameters in relations (5) and (6). A detailed discussion of this problem will be given elsewhere. The calculated values Z_d , given in Table I, show a divergence analogous to that of the values of Z_d , because of some supplementary influence exerted by small differences of the evaporation entropies of the homologues.

I wish to express my thanks to Professor W. Świątosławski for his help and assistance.

1	2	3	4	5	6	7	8	9	10	11
		components	t_A or t_{Hi}	ΔS	t_{Az}	Z_d	Z_g	$\frac{1}{2} Z$	ΔZ_d	Z_m
I	A	methanol	64.65	25.09						
	1	isopentane	27.95	19.41	24.55	63.3	81.8	66.9	+1.1	
	2	<i>n</i> -pentane	36.15	19.92	30.8	62.2	78.3	66.2	0.0	
	3	diisopropyle	58.0	19.68	45.0	58.1	74.1	64.6	-4.1	
	4	<i>n</i> -hexane	68.8	20.17	50.5	57.7	71.7	64.6	-4.5	
	5	<i>n</i> -heptane	98.4	20.38	59.1	64.5	79.5	74.9	+2.3	
	6	isooctane	99.3	19.90	59.4	62.7	79.0	74.1	+0.5	
	7	diisobutyle	109.4	20.44	61.0	67.1	82.3	78.6	+4.9	
	8	<i>n</i> -octane	125.75	20.59	63.0	71.5	87.1	84.6	+9.3	62.2
II	1	benzene	80.1	20.81	58.34	49.2	59.3	55.4	-1.3	
	2	toluene	110.75	20.85	63.75	51.9	62.4	60.9	+1.4	50.5
III	1	methylcyclopentane . . .	72.0	20.05	51.3	59.6	74.6	67.3	2.6	
	2	cyclohexane	80.75	20.30	54.2	61.8	76.4	70.2	-0.4	
	3	methylcyclohexane . . .	101.15	20.26	59.45	65.3	80.8	76.4	+3.1	62.2
IV	A	ethanol	78.3	27.72						
	1	isopentane	27.95	19.41	26.75	65.3	93.4	68.5	+8.7	
	2	<i>n</i> -pentane	36.15	19.92	34.2	61.3	85.2	64.6	+4.7	
	3	diisopropyle	58.0	19.68	51.5	53.7	75.6	59.7	-0.9	
	4	<i>n</i> -hexane	68.8	20.17	58.68	51.0	70.1	57.9	-3.6	
	5	<i>n</i> -heptane	98.4	20.38	70.9	52.1	70.8	63.4	-2.5	
	6	diisobutyle	109.4	20.44	73.2	55.1	74.8	68.5	+0.5	
	7	<i>n</i> -octane	125.75	20.59	76.3	54.3	73.1	69.3	-0.3	54.6
V	1	benzene	80.1	20.81	68.24	38.3	51.0	44.1	-1.0	
	2	toluene	110.75	20.85	76.65	40.3	53.6	50.8	+1.0	39.3
VI	1	methylcyclopentane . . .	72.0	20.05	60.3	51.2	70.7	58.7	+0.1	
	2	cyclohexane	80.75	20.30	64.9	50.0	68.3	58.4	-1.1	
	3	methylcyclohexane . . .	101.15	20.26	71.95	52.0	69.1	62.8	+0.9	51.1
VII	A	propanol-1	97.2	26.63						
	1	<i>n</i> -hexane	68.8	20.17	65.65	51.2	67.6	54.5	+5.8	
	2	<i>n</i> -heptane	98.4	20.38	84.8	45.5	59.5	52.0	+0.1	
	3	diisobutyle	109.4	20.44	89.5	44.7	58.2	52.4	-0.7	
	4	<i>n</i> -octane	125.75	20.59	93.9	46.0	59.5	55.7	+0.6	45.4
VIII	1	methylcyclopentane . . .	72.0	20.05	68.5	48.7	64.7	52.2	+1.9	
	2	cyclohexane	80.75	20.30	74.3	49.0	64.3	53.7	+2.2	
	3	methylcyclohexane . . .	101.15	20.26	86.0	45.5	59.8	52.5	-1.3	
	4	dimethylcyclohexane-1, 3	120.7	20.25	93.0	44.0	57.9	53.5	-2.8	46.8
IX	1	benzene	80.1	20.81	77.12	37.0	46.6	38.9	+0.5	
	2	toluene	110.75	20.85	92.35	36.0	46.0	42.1	-0.5	36.5

L E I

1	2	3	4	5	6	7	8	9	10	11
		components	t_A or t_{Hi}	ΔS	t_{Az}	Z_d	Z_g	$\frac{1}{2}Z$	ΔZ_d	Z_m
X	A	butanol-1	117.8	26.16						
	1	<i>n</i> -heptane	98.4	20.38	93.95	45.6	58.5	49.0	+3.6	42.0
	2	diisobutyle	109.4	20.44	101.9	41.0	52.5	45.2	-1.0	
	3	<i>n</i> -octane	125.75	20.59	110.2	39.3	49.9	45.1	-2.7	
	1	toluene	110.75	20.85	105.7	30.1	37.7	32.8	—	
XI	1	methylcyclopentane . . .	72.0	20.05	71.8	51.4	67.1	52.3	+3.6	47.8
	2	cyclohexane	80.75	20.30	79.8	49.3	63.5	51.0	+1.5	
	3	methylcyclohexane . . .	101.15	20.26	96.4	42.8	55.3	46.3	-5.0	
	4	dimethylcyclohexane . .	120.7	20.25	108.5	37.5	48.4	42.8	-10.3	
XII	A	isopropanol	82.4	26.46						
	1	<i>n</i> -hexane	68.8	20.17	62.3	45.0	59.0	49.5	+0.4	44.6
	2	<i>n</i> -heptane	98.4	20.38	76.4	43.1	55.9	51.0	-1.5	
	3	diisobutyle	109.4	20.44	78.8	45.7	59.2	55.2	+1.1	
	4	<i>n</i> -octane	125.75	20.59	81.6	44.7	57.4	55.7	+0.1	
XIII	1	methylcyclopentane . . .	72.0	20.05	63.3	48.2	63.5	53.6	+3.0	45.2
	2	cyclohexane	80.75	20.30	68.6	45.7	59.6	51.8	+0.5	
	3	methylcyclohexane . . .	101.15	20.26	77.4	42.2	55.1	50.5	-3.0	
	4	dimethylcyclohexane-1, 3	120.7	20.25	81.0	44.8	58.5	56.0	-0.4	
XIV	1	benzene	80.1	20.81	71.92	33.5	42.7	37.4	-0.4	33.9
	2	toluene	110.75	20.85	81.3	34.4	43.7	41.9	+0.5	
XV	A	methyl formate	31.7	23.79						
	1	isopentane	27.95	19.41	17.05	46.4	56.9	50.8	+1.2	45.2
	2	<i>n</i> -pentane	36.15	19.92	21.8	43.7	52.2	48.1	-1.1	
	3	diisopropyle	58.0	19.68	30.5	34.4	41.6	40.2	-10.8	
XVI	A	ethyl formate	54.15	22.66						
	1	isopentane	27.95	19.41	27.6	37.6	43.9	38.3	-1.1	38.7
	2	<i>n</i> -pentane	36.15	19.92	33.5	36.8	41.9	38.1	-1.9	
	3	diisopropyle	58.0	19.68	45.0	40.8	47.0	44.0	+2.1	
	4	<i>n</i> -hexane	68.8	20.17	49.5	39.7	44.6	42.9	+1.0	
XVII	A	propyl acetate	101.6	22.14						
	1	<i>n</i> -heptane	98.4	20.38	93.6	24.8	25.7	25.2	-1.3	26.1
	2	diisobutyle	109.4	20.44	98.0	27.3	28.2	27.8	+1.2	
XVIII	A	propyl formate	80.85	21.20						
	1	diisopropyle	58.0	19.68	56.2	39.2	42.2	39.8	+0.4	38.8
	2	<i>n</i> -hexane	68.8	20.17	63.6	40.7	42.8	41.4	+1.9	
	3	<i>n</i> -heptane	98.4	20.38	78.2	36.4	37.9	37.4	-2.4	
XIX	A	methyl butyrate	102.65	21.81						
	1	<i>n</i> -heptane	98.4	20.38	95.1	20.3	21.7	20.8	0.0	20.05
	2	diisobutyle	109.4	20.44	100.0	20.2	21.6	22.0	0.0	

Summary

1. According to Świętosławski's [1], [2], [3], [4] scheme of formation of the series of binary azeotropes of the agent A with the representatives of a homologous series (H), the case has been considered when the upper portion Z_g and the lower portion Z_d of the azeotropic range Z are not equal. In that case the azeotropic range is asymmetrical.

2. It has been shown that the ratio of the two portions of the ranges Z is equal to the ratio of evaporation entropies:

$$(3) \quad \frac{Z_d}{Z_g} = \frac{\Delta S_H}{\Delta S_A}.$$

3. Equations have been derived, which determine the composition (expressed in mole fractions x_A and x_{H_i}) and the azeotropic depression ($\delta_A = T_A - T_{Az}$; $\delta_{H_i} = T_{H_i} - T_{Az}$) in the series of azeotropes mentioned, characterised by asymmetrical ranges. The equations are expressed as follows:

$$(10a) \quad \Delta H_i = -Z_d + 2\sqrt{Z_d}\sqrt{\delta_{H_i}}\sqrt{\frac{\Delta S_H}{\Delta S_A}} + \delta_{H_i}\left(1 - \frac{\Delta S_H}{\Delta S_A}\right)$$

$$(14) \quad x_{H_i} = \frac{1}{2} + \frac{\Delta_A}{2Z_g} + \frac{x_{H_i}^2}{2}\left(1 - \frac{\Delta S_H}{\Delta S_A}\right)$$

where Δ_A and Δ_{H_i} denote the boiling temperature differences of the components ($\Delta_A = T_A - T_{H_i}$; $\Delta_{H_i} = T_{H_i} - T_A$).

4. The values of the azeotropic ranges have been calculated from the data given for systems formed for 16 azeotropic agents (alcohols and esters) with series of paraffinic, naphthenic and aromatic hydrocarbons. The equations

$$(5) \quad Z_d = \left(\sqrt{\delta_A} + \sqrt{\delta_{H_i}}\sqrt{\frac{\Delta S_H}{\Delta S_A}}\right)^2$$

$$(6) \quad Z_g = \left(\sqrt{\delta_A}\sqrt{\frac{\Delta S_A}{\Delta S_H}} + \sqrt{\delta_{H_i}}\right)^2$$

were used.

In this way a satisfactory agreement has been found: for a given series of azeotropes (ΔH_i), values of Z_d and Z_g , approximately constant, have been obtained.

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On the Relation Between the Azeotropic Ranges and the Binary Regular Solution Constants in Three-Component Systems

by

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1. Introductory remarks. The purpose of this paper is to determine the relation between the values of the azeotropic ranges and regular solution constants A_{12} , A_{23} and A_{13} for the case when the components 1, 2 and 3 form a three-component homogenous solution. The constants A_{ij} are defined by the equations determining the activity coefficients f_i and f_j of the components for the separate binary solutions under the isobaric equilibrium with the vapour phase as follows:

$$(1a) \quad RT \ln f_i = A_{ij} x_j^2,$$

$$(1b) \quad RT \ln f_j = A_{ij} x_i^2,$$

where R denotes the gas constant, T — the absolute temperature, and x_i , x_j — the mole fractions of the components i and j in a binary mixture.

2. Ternary tangent azeotropes. The formation of ternary tangent azeotropes has been taken into account by Świetoslawski [1]-[4] in his scheme of the formation of positive azeotropes. According to this scheme, in the case when an upper tangent azeotrope is formed by azeotropic agent A and homologue H_k (Fig. 1a), then in the ternary system (A, B, H_k) there exists a ternary tangent azeotrope, characterised by an extremely small content of H_k , as presented both in Fig. 1b and in the three-dimensional diagram (Fig. 2). The system presented in Fig. 2 is characterised by a boiling temperature isobar AH_k , tangent at point T_A , and also by an isobar of mixtures of the azeotropes (A, B) and (B, H_k) , being tangent at point $T_{A,B}$ to the constant temperature (horizontal) plane $T = T_{A,B}$. Therefore, the azeotrope (A, B) as well as the ternary tangent azeotrope (A, B, H_k) are identical. Consequently various mixtures of A, H_k

or B, H_k with the azeotropic one (A, B) will form isobars tangent to the same horizontal plane drawn through $T = T_{A,B}$. The boiling temperature isobar of azeotrope (A, B) with H_k will also be tangent.

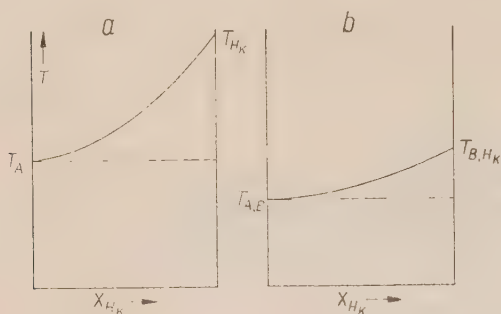


Fig. 1

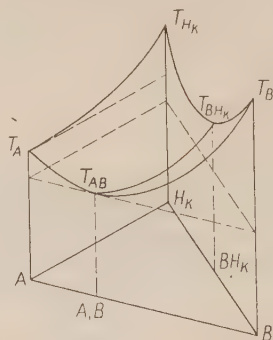


Fig. 2

Fig. 1 (a) The tangent boiling temperature isobar of mixtures of the azeotropic agent A with H_k . — (b) The tangent boiling temperature isobar of mixtures of the azeotrope (A, B) with the azeotrope (B, H_k)

Fig. 2. Ternary tangent azeotrope (A, B, H_k)

3. Ternary azeotrope tangent at the triangle corner. According to the above considerations, if not only the (A, H_k) but also the (A, B) azeotrope is tangent at the point corresponding to the limiting composition $x_B = 1$, then the ternary tangent azeotrope will lie at the same point in the triangle corner $x_B = 1$. It follows that azeotrope (B, H_k) will be tangent at the same limiting composition. Such

a particular case of a system characterised only by tangent azeotropes: one ternary and three binary is shown in Fig. 3.

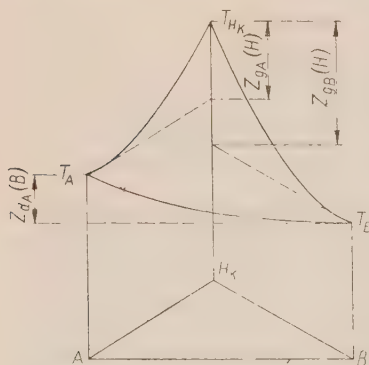


Fig. 3. Ternary tangent azeotrope characterised by the limiting composition $x_B = 1$

Therefore, the fundamental conclusion reached by the consideration of Świątosławski's scheme is that such ternary tangent azeotropes should be formed, as would be characterised by three binary tangent azeotropes, provided the boiling temperatures of the components fulfill certain required conditions. This conclusion will be the basis of our further considerations.

4. Relation between the binary azeotropic ranges in the ternary system.

Suppose that the azeotropic agent A will form azeotropes with the representatives of homologous series (H) and (B). Then, in the case shown in Fig. 3, the sum of the upper portion of the azeotropic range of agent A in relation to series (H), and that of the lower portion of the range

in relation to series (*B*), is equal to the upper portion of the range of agent *B* in relation to series (*H*). This may be written as follows:

$$(2) \quad Z_{g_A}(H) + Z_{d_A}(B) = Z_{g_B}(H),$$

or, using the following simplified subscripts: *H* — “1”, *A* — “2”, *B* — “3”, and $Z_{g_A}(H) \equiv Z_{g_{21}}$, $Z_{d_A}(B) \equiv Z_{d_{23}}$, $Z_{g_B}(H) \equiv Z_{g_{31}}$, we obtain:

$$(3) \quad Z_{g_{21}} + Z_{d_{23}} = Z_{g_{31}}.$$

If we assume that the azeotropic ranges are symmetrical [5], [6], i. e.

$$Z_{g_{ij}} = Z_{g_{ji}} = \frac{1}{2} Z_{ij} = \frac{1}{2} Z_{ji},$$

equation (3) transforms into the relation:

$$(4) \quad Z_{12} + Z_{23} = Z_{13}.$$

5. Relation between the regular solution constants in the three-component system. It has been previously shown [5], [6], that the values of the upper and lower portions of the azeotropic range of agent *A* in relation to series (*H*) depend on the regular solution constant A_{AH} . This is expressed by the equations

$$(5) \quad Z_d = \frac{A_{AH}}{\Delta S_A}, \quad Z_g = \frac{A_{AH}}{\Delta S_H},$$

ΔS_A and ΔS_H being the respective vaporisation entropies at the boiling temperatures of the agent *A* and of the representatives of series (*H*). Equations (5) may be written in a general form as follows:

$$(6) \quad Z_{d_{ij}} = \frac{A_{ij}}{\Delta S_i}, \quad Z_{g_{ij}} = \frac{A_{ij}}{\Delta S_j}.$$

Because A_{ij} is equal to A_{ji} , we have $Z_{d_{ij}} = Z_{g_{ji}}$. Consequently, equation (3) may be expressed in the following manner:

$$(7) \quad \frac{A_{12}}{\Delta S_1} + \frac{A_{23}}{\Delta S_2} = \frac{A_{13}}{\Delta S_1}.$$

If $\Delta S_1 = \Delta S_2$, a further simplification results:

$$(8) \quad A_{12} + A_{23} = A_{13}.$$

The relation (8) may be considered as a fundamental one, although it was derived on the basis of the empirical relation (2) and of the assumption that the vaporisation entropies of the components are equal. It is clear that in the case of identical vaporisation entropies (i. e. of the symmetrical azeotropic ranges), relations (2) and (8) are equivalent.

The unexpected simplicity of relation (8) may become more evident, if the fact is taken under consideration that it correlates the constants A , determined by the activity coefficients of the components of binary mixtures in the state of an isobaric equilibrium, with the corresponding vapour phases. The constants A are determined by the parameters of the azeotropic mixtures at their respective boiling points at constant pressure, which means that these mixtures are in a certain kind of corresponding state.

It is possible to correlate the constants A_{12} , A_{23} and A_{13} on the basis of the generally accepted approximation [7]:

$$(9) \quad c_{12} = \sqrt{c_{11} \cdot c_{22}},$$

where c are the parameters determining the dispersion energy of the interacting molecules. A_{ij} is given by the equation

$$(10) \quad A_{ij} = (c_{ii}^{1/2} - c_{jj}^{1/2})^2;$$

therefore

$$(11) \quad \sqrt{A_{12}} + \sqrt{A_{23}} = \sqrt{A_{13}}.$$

Equation (11) is inconsistent with (8), which leads to great differences in the numerical results. If, for example, A_{12} is equal to 400 cal., and A_{23} to 900 cal., then A_{13} , according to (11) would be equal to 2500 cal., and according to (8) to 1300 cal. Since relation (8) gives satisfactory agreement with experimental data (Table I), relation (11) is not applicable for our purposes. The constants A in relation (11) are associated rather with the heat of mixing, instead of with the excess free energy, as in the case of constants A in relation (8). As mentioned above they correspond to the isobaric conditions.

6. The application limits and the experimental verification of relation (8).

Since relation (8) was derived for the regular solutions, in which the molecular interaction is due to dispersion forces only, a poor agreement with experimental data might be expected for systems in which the specific interactions between unlike molecules take place, as, for example, hydrogen bond formation. Therefore, the application of (8) is limited to systems composed of two nonpolar substances, and a third one, which may be characterised by some polarity. In addition, an approximation is introduced, consisting in the equality of the vaporisation entropies of the components. In this case, relation (4) may be applied in the following form:

$$(12) \quad \frac{1}{2}Z_{12} = \frac{1}{2}Z_{13} - \frac{1}{2}Z_{23}.$$

The values of $\frac{1}{2}Z_{ij}$ are determined by the experimental azeotropic parameters with the aid of the equation previously derived [5], [6]:

$$(13) \quad \frac{1}{2}Z_{ij} = (\sqrt{\delta_j} + \sqrt{\delta_i})^2 \quad \text{or} \quad A_i = -\frac{1}{2}Z + \sqrt{2Z}\sqrt{\delta_i}.$$

TABLE I

No. syst.	Components	System—(1,3)			System —(2,3)			$\frac{1}{2}Z_{13}-\frac{1}{2}Z_{23}$	ΔZ
		Δ	δ	$\frac{1}{2}Z_{13}$	Δ	δ	$\frac{1}{2}Z_{23}$		
(1) heptane — (2) benzene $\Delta=18.2$ $\delta=0$ $\frac{1}{2}Z=18.2$									
1	methanol	33.75	5.65	75.0	15.38	7.22	55.0	20.0	+1.8
2	ethanol	20.15	7.4	63.0	1.8	10.6	43.5	19.5	+1.3
3	propanol-2	16.0	6.0	51.0	2.25	8.28	37.0	14.0	-4.2
4	2-methyl-propanol-2 . .	15.95	4.45	45.0	2.35	6.25	29.0	16.0	-2.2
5	allyl alcohol	1.55	12.5	52.0	16.75	3.3	39.0	13.0	-5.2
6	propanol-1	1.2	12.4	52.0	17.0	3.08	39.0	13.0	-5.2
7	butanol-2	1.1	10.0	42.0	19.35	1.6	34.0	8.0	-10.2
8	2-methyl-propanol-1 . .	9.6	7.3	46.5	27.85	0.36	35.0	11.5	-6.7
9	formic acid	2.35	20.2	86.0	20.6	9.1	72.0	14.0	-4.2
10	acetic acid	19.7	6.1	57.0	37.95	0.13	45.0	12.0	-6.2
(1) cyclohexane — (2) benzene $\Delta=0.6$ $\delta=2.4$ $\frac{1}{2}Z=11$									
11	methanol	16.1	10.45	70.0	15.38	7.22	55.0	15.0	+4.0
12	ethanol	2.45	13.4	58.0	1.8	10.6	43.5	14.5	+3.5
13	propanol-2	1.65	12.15	52.0	2.25	8.28	37.0	15.0	+4.0
14	2-methyl-propanol-2 . .	1.7	9.3	40.0	2.35	6.25	29.0	11.0	0.0
15	allyl alcohol	16.1	6.65	54.0	16.75	3.3	39.0	15.0	+4.0
16	propanol-1	16.45	6.45	54.0	17.0	3.08	39.0	15.0	+4.0
17	butanol-2	18.75	4.25	47.0	19.35	1.6	34.0	13.0	+2.0
18	2-methyl-propanol-1 . .	27.25	2.6	50.0	27.85	0.36	35.0	15.0	+4.0
19	formic acid	20.0	11.25	80.0	20.6	9.1	72.0	8.0	-3.0
20	acetic acid	37.35	1.05	52.0	37.95	0.13	45.0	7.0	-4.0
(1) heptane — methylcyclohexane $\Delta=2.75$ $\delta=0.02$ $\frac{1}{2}Z=2.7$									
21	methanol	33.75	5.65	75.0	36.5	5.2	76.0	-1.0	-3.7
22	ethanol	20.15	7.4	63.0	22.85	6.35	62.5	+0.5	-2.2
23	propanol-2	16.0	6.0	51.0	18.75	5.0	50.5	+0.5	-2.2
24	2-methyl-propanol-2 . .	15.95	4.45	45.0	18.7	4.45	48.0	-3.0	-5.7
25	allyl alcohol	1.55	12.5	52.0	4.3	11.05	52.0	0.0	-2.7
26	propanol-1	1.2	12.4	52.0	3.95	11.2	52.5	-0.5	-3.2
27	butanol-2	1.1	10.0	42.0	1.65	9.7	42.0	0.0	-2.7
28	2-methyl-butanol-2 . . .	3.95	6.25	32.5	1.2	7.82	33.5	-1.0	-3.7
29	2-methyl-propanol-1 . .	9.6	7.3	46.5	6.85	7.85	44.0	+2.5	-0.2
30	2-methyl-butanol-3 . . .	14.5	3.4	37.0	11.75	4.15	37.0	0.0	-2.7
31	pentanol-3	17.6	2.4	36.0	14.85	3.35	37.0	-1.0	-3.7
32	butanol-1	19.4	4.45	49.0	16.65	4.75	46.5	+2.5	-0.2
33	pentanol-2	21.4	2.4	42.5	18.65	2.55	38.5	+4.0	+1.3
34	butanone-2	18.8	2.6	39.0	21.55	1.9	38.0	+1.0	-1.7
35	pentanone-3	3.65	5.4	28.5	0.9	6.15	26.5	+2.0	-0.7
36	2-methyl-butanone-3 . .	3.95	5.2	28.0	1.2	5.92	26.0	+2.0	-0.7
37	pinacolin	7.8	2.9	25.0	5.05	4.15	25.5	-0.5	-3.2
38	2-methyl-pentanone-4 . .	17.65	0.9	27.5	14.9	1.05	25.0	+2.5	-0.2
39	propyl formate	17.55	2.65	37.5	20.3	0.65	29.0	+8.5	+5.8
40	ethyl nitrate	10.7	4.9	38.0	13.45	3.85	37.5	+0.5	-2.2

No. syst.	Components	System —(1,3)			System —(2,3)			$\frac{1}{2}Z_{13} \rightarrow \frac{1}{2}Z_{23}$	ΔZ
		Δ	δ	$\frac{1}{2}Z_{13}$	Δ	δ	$\frac{1}{2}Z_{23}$		

(1) heptane — methyleyclohexane $\Delta = 2.75$ $\delta = 0.02$ $\frac{1}{2}Z = 2.7$

41	methyl carbonate	8.15	8.0	47.0	10.9	5.25	40.0	+7.0	+4.3
42	methyl isobutyrate	5.9	2.8	21.5	8.65	1.8	21.0	+0.5	-2.2
43	isoamyl nitrate	1.25	2.35	12.0	4.0	1.65	13.5	-1.5	-4.2
45	isobutyl formate	0.2	7.7	31.0	2.95	5.7	28.5	+2.5	-0.2
46	ethyl propionate	0.7	5.4	23.0	2.05	4.3	22.0	+1.0	-1.7
47	methyl butyrate	4.25	3.3	21.0	1.5	4.15	19.5	+1.5	-1.2
48	ethyl isobutyrate	11.7	1.4	23.0	8.95	1.45	19.5	+3.5	+0.8
49	propyl nitrate	12.1	3.4	33.5	9.35	4.15	32.5	+1.0	-1.7
50	isoamyl chloride	1.0	1.9	9.5	1.75	1.4	8.5	+1.0	-1.7
51	butyl bromide	3.1	1.4	11.0	0.35	1.65	7.0	4.0	+1.3
52	allyl iodide	3.4	1.4	11.5	0.65	1.95	9.0	2.5	-0.2
53	isobutyl cyanide	5.45	17.9	82.0	2.7	15.65	78.0	+4.0	+1.3
54	nitro methane	2.8	18.2	78.0	0.05	19.9	79.0	-1.0	-3.7
55	nitro ethane	15.8	9.2	64.5	13.05	10.35	63.0	+1.5	-1.2
56	chloro-pierin	13.5	0.08	16.0	10.75	0.35	15.5	+0.5	-2.2
57	dioxane	2.95	6.55	32.0	0.2	7.65	31.0	+1.0	-1.7
58	acetal	5.15	0.65	10.5	2.4	1.5	10.5	0.0	-2.7
59	epichlorohydrin	18.8	0.3	24.0	15.25	0.35	20.5	+3.5	+0.8

(1) diisobutyl — (2) toluene $\Delta = 1.35$ $\delta = 2.4$ $\frac{1}{2}Z = 12.0$

60	methanol	44.75	3.65	78.5	46.1	0.9	60.0	18.5	+6.5
61	ethanol	31.1	5.1	68.0	32.45	1.65	51.0	17.0	+5.0
62	allyl alcohol	12.55	7.55	52.0	13.9	4.55	40.0	12.0	0.0
63	propanol-1	12.2	7.7	52.0	13.55	4.85	47.5	9.5	-2.5
64	butanol-2	9.9	6.5	43.5	11.25	4.0	35.0	8.5	-3.5
65	2-methyl-butanol-2	7.05	5.35	34.0	8.4	2.95	26.0	8.0	-4.0
66	2-methyl-propanol-1	1.4	9.8	42.0	2.75	6.9	33.0	9.0	-3.0
67	butanol-1	8.4	7.5	45.0	7.05	5.05	33.0	12.0	0.0
68	2-methyl-butanol-4	22.5	1.8	39.0	21.15	0.7	30.0	9.0	-3.0
69	formic acid	8.65	17.55	87.0	10.0	14.95	79.0	8.0	-4.0
70	acetic acid	8.7	8.9	51.0	7.35	5.8	40.0	11.0	-1.0
71	propionic acid	31.9	1.4	47.0	30.55	0.3	37.0	10.0	-2.0
72	1-chloro-propanol-2	17.6	4.4	47.0	16.25	1.75	31.0	16.0	+4.0
73	chloroethanol	19.2	8.4	66.0	17.85	3.8	43.5	22.5	+10.5
74	propandiol-1, 2	15.1	9.4	64.0	13.75	4.65	40.0	24.0	+12.0
75	butandiol-1, 2	25.9	4.4	58.0	24.55	0.6	33.5	24.5	+12.5
76	methyl lactate	34.4	0.9	47.5	33.05	0.15	40.0	7.5	-4.5
78	nitro methane	8.2	15.7	78.0	9.55	4.7	35.0	43.0	+31.0
79	nitro ethane	4.8	12.5	59.5	3.45	4.55	24.5	35.0	+23.0
80	epichlorhydrin	7.0	2.9	23.5	5.65	2.35	19.0	4.5	-7.5
81	pyridine	6.0	3.9	26.0	4.65	0.6	9.5	16.5	+4.5

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No. syst.	Components	System —(1,3)			System —(2,3)			$\frac{1}{2}Z_{13}$ — $\frac{1}{2}Z_{23}$	AZ
		Δ	δ	$\frac{1}{2}Z_{13}$	Δ	δ	$\frac{1}{2}Z_{23}$		
(1) octane — ethylbenzene $\Delta=10.4$ $\delta=0.15$ $\frac{1}{2}Z=12.5$									
82	formic acid	25.0	10.25	82.5	35.4	6.7	82.5	0.0	—12.5
83	acetic acid	7.65	9.1	50.5	18.05	3.45	42.0	8.5	—4.0
84	propionic acid	15.55	4.25	42.5	5.15	5.05	29.5	13.0	+0.5
85	isobutyric acid	28.85	1.65	46.5	18.45	2.05	35.5	11.0	—1.5
86	butyric acid	38.25	1.25	54.5	27.85	0.35	35.0	18.5	+6.0
87	2-methyl-propanol-1 . .	17.75	5.5	51.5	28.15	0.5	36.5	15.0	+2.5
88	butanol-1	7.95	7.6	45.0	18.35	2.3	36.5	8.5	—4.0
89	pentanol	5.95	5.0	31.0	16.35	1.8	31.0	0.0	—12.5
90	2-methyl-butanol-4 . . .	6.15	5.95	35.0	4.25	5.6	30.5	4.5	—8.0
91	ethanolamine	45.05	2.7	73.5	34.65	5.15	73.0	0.5	—12.0
92	methyl lactate	18.05	5.45	51.5	7.65	7.5	44.0	7.5	—5.0
93	chloroethanol	2.85	13.25	58.5	7.55	7.6	44.5	12.0	—0.5
94	propandiol-1, 2	1.25	14.5	60.0	11.65	5.7	43.0	17.0	+4.5
95	butandiol-1, 2	9.55	9.75	57.0	0.85	7.5	45.5	11.5	—1.0
96	acetamide	95.4	0.25	106.0	85.0	0.65	101.0	5.0	—7.5
97	methylchloroacetate . . .	4.2	4.25	25.0	6.2	2.75	21.5	3.5	—9.0
98	methyl-glycol acetate . .	18.25	0.55	25.5	8.45	0.65	14.5	11.0	—1.5

(1) diisooamyl — (2) mesithylene $\Delta=4.5$ $\delta=1.5$ $\frac{1}{2}Z=13.5$

99	formic acid	59.35	2.25	87.0	63.85	1.05	82.0	5.0	-7.5
100	propionic acid	18.8	3.3	42.5	23.3	0.3	29.5	13.0	-0.5
101	isobutyric acid	5.5	6.6	36.5	10.0	3.1	29.0	7.5	-6.0
102	butyric acid	3.9	7.6	38.0	0.6	6.0	25.0	13.0	-0.5
103	isovalerianic acid	16.4	2.1	33.0	11.9	2.1	26.0	7.0	-6.5
104	chloroacetic acid	28.25	4.4	61.0	24.75	4.1	54.0	6.0	-7.5
105	hexanol-1	2.25	5.85	28.0	6.75	2.75	22.5	5.5	-8.0
106	cyclohexanol	0.7	7.3	30.5	3.8	4.4	24.5	6.0	-7.5
107	methyl-cyclohexanol-1, 2	8.4	4.3	32.0	3.9	4.1	23.5	8.5	-5.0
108	methyl lactate	16.3	6.0	51.5	20.8	2.8	42.5	9.0	-4.5
109	propandiol-1, 2	35.6	3.5	66.0	40.1	0.2	46.0	20.0	+6.5
110	pentandiol-1, 2	8.7	7.65	46.0	13.25	1.95	28.0	18.0	+4.5
111	ethyl acetylacetate	20.3	4.1	48.5	15.8	2.1	32.0	16.5	+3.0
112	methyl malonate	21.3	4.6	52.5	16.8	1.6	31.0	21.5	+8.0

(1) α -pinene — (2) isopropylbenzene $\Delta=3.0$ $\delta=1.0$ $\frac{1}{2}Z=9.0$

113	propionic acid	14.5	5.0	43.5	11.5	2.3	27.5	16.0	+7.0
114	isobutyric acid	1.2	7.8	33.5	1.8	6.0	27.5	6.0	-3.0
115	butyric acid	8.2	5.6	37.0	11.2	3.3	32.0	5.0	-4.0
116	isovalerianic acid	20.7	1.6	36.0	23.7	0.8	34.0	2.0	-7.0
117	valerianic acid	30.55	0.3	37.0	27.05	0.9	39.0	-1.0	-10.0

TABLE I

continued

No. syst.	Components	System —(1,3)			System —(2,3)			$\frac{1}{2}Z_{13}-\frac{1}{2}Z_{23}$	AZ
		Δ	δ	$\frac{1}{2}Z_{13}$	Δ	δ	$\frac{1}{2}Z_{23}$		
(1) α -pinene — (2) isopropylbenzene $\Delta=3.0$ $\delta=1.0$ $\frac{1}{2}Z=9.0$									
118	chloroacetic acid	33.55	4.2	67.0	36.55	0.0	58.0	9.0	0.0
119	isobutylcarbinol	23.9	1.2	37.0	20.9	0.35	27.0	10.0	+1.0
120	hexanol-1	2.05	5.8	27.0	5.05	3.3	22.0	5.0	—5.0
121	cyclohexanol	5.0	5.9	33.0	8.0	2.8	24.5	8.5	—0.5
122	methyl-cyclohexanol-1, 2	12.7	3.0	32.5	15.7	11.0	26.5	6.0	—3.0
123	glycol	41.6	6.3	89.0	44.6	5.8	90.5	—1.5	—10.5
124	ethanolamine	15.0	13.8	82.5	18.0	10.3	73.0	9.5	+0.5
125	methyl lactate	12.0	8.3	54.5	9.0	6.0	40.0	14.5	+5.5
126	ethyl lactate	1.7	11.0	47.0	5.2	6.1	34.0	13.0	+4.0
127	butandiol-1, 2	20.5	4.3	50.0	17.5	2.1	34.5	15.5	+6.5
128	furfural	5.65	12.4	60.5	8.65	4.3	32.0	28.5	+19.5
129	acetamide	65.35	3.3	102.0	68.35	2.0	97.0	5.0	+4.0
130	propionic acid amide . . .	66.0	1.8	104.0	69.0	1.0	88.0	16.0	+7.0
131	cyclohexanone	0.1	6.0	24.0	2.9	0.8	8.0	16.0	+7.0
132	methyl-glycol acetate . .	11.2	2.6	28.5	8.2	0.3	11.0	17.5	+8.5
(1) triethylbenzene-1, 2, 4 — (2) naphthalene $\Delta=2.5$ $\delta=0.7$ $\frac{1}{2}Z=7$									
133	caprylic acid	10.35	3.15	30.0	12.85	1.4	24.5	5.5	—1.5
134	heptanoic acid	6.5	4.5	29.5	4.0	3.8	22.5	7.0	0.0
135	chloroacetic acid	26.15	3.85	55.5	28.7	2.25	50.0	5.5	—1.5
136	bromoacetic acid	10.4	6.1	42.5	12.9	3.8	36.5	6.0	—1.0
137	glycol	18.1	14.9	92.0	20.6	13.5	90.5	1.5	—5.5
138	benzyl alcohol	10.25	3.15	29.5	12.75	1.1	22.5	7.0	0.0
139	borneol	0.5	2.3	10.0	3.0	0.6	7.0	3.0	—4.0
140	menthol	0.8	2.0	9.5	1.7	1.25	8.0	1.5	—5.5
141	benzyl-carbinol	3.9	3.0	19.0	1.4	3.8	18.0	1.0	—6.0
142	citronellol	8.9	0.2	12.0	6.4	0.2	9.0	3.0	—4.0
143	glicerol	75.0	2.7	112.0	72.5	2.8	107.0	5.0	—2.0
144	methyl-diglycol	22.55	2.95	46.0	25.05	0.75	35.5	11.0	+4.0
145	methyl-triglycol	29.75	3.5	58.5	27.25	3.2	53.5	5.0	—2.0
146	acetamide	5.65	17.5	81.0	3.15	18.45	80.0	1.0	—6.0
147	diglycol	30.0	6.5	74.0	27.5	5.4	64.0	10.0	+3.0
148	<i>o</i> -amino-anisole	3.5	1.0	10.0	1.0	1.0	6.0	4.0	—3.0
149	<i>p</i> -ethyl-phenol	3.3	3.5	20.0	0.8	3.0	13.0	7.0	0.0
150	mesitol	5.0	2.5	29.0	2.5	2.5	15.0	14.0	+7.0
151	pyrocatechol	30.4	0.8	42.0	27.9	0.6	37.0	5.0	—2.0
152	<i>p</i> -chloro-phenol	4.25	0.8	10.0	1.75	1.7	10.0	0.0	—7.0
153	<i>o</i> -nitro-phenol	1.7	1.2	8.0	0.8	1.5	7.0	1.0	—6.0

Thus equations (12) and (8) may be verified, although the latter in an approximate manner only. In the exact verification of (8), and the determination of the constants A , which will be given elsewhere, the asymmetry of the azeotropic ranges should be taken into account as required previously [8].

Table I comprises 153 systems of three components, which form with one another binary azeotropes. In the successive columns are given: 1) the number of the system; 2) the name of the third component; 3) the empirical azeotropic parameters [9], where Δ denotes the boiling temperature differences of the components, δ —the azeotropic depression, and $\frac{1}{2}Z_{13}$ — the calculated value for the system 1,3 (equation (13)); 4) analogous data for the system 2, 3.

The main pairs of nonpolar components 1 and 2 (aliphatic, aromatic and naphthenic hydrocarbons), forming azeotropes with the third component, are given in the corresponding lines together with their two-component parameters and the $\frac{1}{2}Z_{12}$ values, calculated according to equation (13).

In the fifth column, the calculated values of $\frac{1}{2}Z_{12}$, corresponding to the differences between $\frac{1}{2}Z_{13}$ and $\frac{1}{2}Z_{23}$ (according to equation (12)) are given. The values given in the last column represent the differences ΔZ between the $\frac{1}{2}Z_{12}$ values calculated by using equations (12) and (13).

Although the applicability of the relations was limited by the approximation introduced, nevertheless very satisfactory agreement was obtained. The values of ΔZ , in 67 cases are less than 3°C, in 49 cases they lie between 3° and 6°, and in 11 cases they exceed 10°.

It should be emphasised, that the chemical nature of the third components in the examples quoted in the table varies to a large extent. In many cases, all binary azeotropes cited in Lecat's tables were taken into consideration.

I wish to express my thanks to Professor W. Świątosławski for his help and assistance.

Summary

1. On the basis of Świątosławski's scheme of the formation of tangent ternary azeotropes [1]—[4], a relation between the azeotropic ranges $Z_A(H)$ and $Z_A(B)$ of the agent A with respect to two homologous series (H) and (B) has been derived. The sum of ranges $Z_A(H)$ and $Z_A(B)$ is equal to the range of a representative of the series (B) with respect to series (H), i. e.

$$(4) \quad Z_A(H) + Z_A(B) = Z_B(H),$$

where component A is the main azeotropic agent.

2. It has been shown, starting from the relation (4), that the constants A_{12} , A_{23} and A_{13} of binary regular solutions are correlated in the system of three components 1, 2 and 3 as follows:

$$(8) \quad A_{12} + A_{23} = A_{13}$$

where the constants A_{ij} are defined by

$$RT \ln f_i^{(H)} = A_{ij} x_j^2 \quad (i=1,2,3, j=1,2,3, i \neq j, A_{ij}=A_{ji}).$$

This definition determines the activity coefficients of the i -th component at the boiling temperatures (at $p=\text{const.}$) of the respective binary azeotropes.

3. The values calculated according to equations (4) and (8) were verified on 153 systems of three components, and relatively good agreement was obtained.

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